Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for Repurposing amine and carboxylic acid building blocks with an automatable esterification reaction

Methods Summary

All reactions were conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless stated otherwise. Reactions were set up in an MBraun LABmaster Pro Glove Box (H_2O level <0.1 ppm, O_2 level <0.1 ppm), or using standard Schlenk technique with a glass vacuum manifold connected to an inlet of dry nitrogen gas. Acetonitrile (MeCN) was purified using an MBraun SPS solvent purification system by purging with nitrogen, and then passing the solvent through a column of activated alumina. 1,4-dioxane, *N,N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were purchased as the anhydrous solvents and used as received. Reagents were purchased from Sigma Aldrich, Alfa Aesar, Oakwood Chemical, or TCI Chemical. Liquid primary amines were passed through a plug of basic alumina prior to use in making Katritzky salts. Potassium iodide was ground with a mortar and pestle prior to use. All other chemicals were used as received. Glass 1 dram (Fisher Scientific #03-339-21B) or 2 dram vials (Fisher Scientific #03-339-21D) were used as reaction vessels, fitted with a screw cap and Teflon-coated silicone septa (ChemGlass #CG-4910-02), and magnetic stir bars (Fisher Scientific #14-513-93 or #14-513-65).

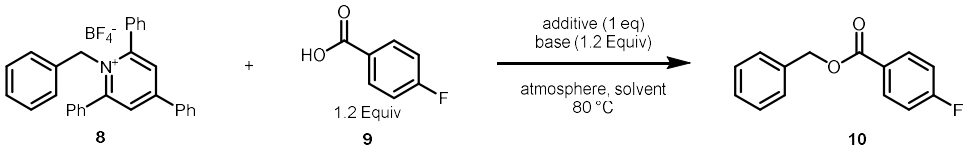
Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian MR-500 MHz, or Varian MR-400 MHz spectrometer and chemical shifts are reported in parts per million (ppm) using the solvent residual peak as an internal standard ($CDCl_3$ at 7.26 ppm, DMSO-d_6 at 2.50 ppm, D_2O at 4.80). Data are reported using the abbreviations: app = apparent, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex, br = broad. Coupling constant(s) are reported in Hz. Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) spectra were recorded on a Varian MR-500 MHz or Varian MR-400 MHz spectrometer and chemical shifts are reported in ppm using the solvent as an internal standard ($CDCl_3$ at 77.16 ppm, DMSO-d_6 at 39.52 ppm). High resolution mass spectrometry data (HRMS) was obtained on a Micromass AutoSpec Ultima Magnetic Sector instrument. Reaction analysis was typically performed by thin-layer chromatography (TLC) on silica gel 60 F_{254} glass plates (Fisher Scientific #S07876) and visualized using ultraviolet light (254 nm), ninhydrin stain, or potassium permanganate ($KMnO_4$) stain; or using a Waters I-class ACQUITY UPLC-MS (Waters Corporation, Milford, MA, USA) equipped with in-line photodiode array detector (PDA) and QDa mass detector (ESI positive ionization mode). 0.1 µL sample injections were taken from acetonitrile solutions of reaction mixtures or products (~1 mg/mL). A partial loop injection mode was used with the needle placement at 1.0 mm from bottom of the wells and a 0.2 µL air gap at pre-aspiration and post-aspiration. Column used: Waters Cortecs UPLC C18+ column, 2.1mm · 50 mm with (Waters #186007114) with Waters Cortecs UPLC C18+ VanGuard Pre-column 2.1mm · 5 mm (Waters #186007125), Mobile Phase A: 0.1 % formic acid in Optima LC/MS-grade water, Mobile Phase B: 0.1% formic acid in Optima LC/MS-grade MeCN. Flow rate: 0.8 mL/min. Column temperature: 45 °C. The PDA sampling rate was 20 points/sec. The QDa detector monitored m/z 150-750 with a scan time of 0.06 seconds and a cone voltage of 30 V. The PDA detector range was between 210 nm – 400 nm with a resolution of 1.2 nm. 1-minute and 2-minute methods were used. The method gradients are as follows: 0 min: 0.8 mL/ min, 95% 0.1% formic acid in water/ 5% 0.1% formic acid in acetonitrile; 1.5 min: 0.8 mL/ min, 0.1% 0.1% formic acid in water/ 99.9% 0.1% formic acid in acetonitrile; 1.91 min: 0.8 mL/min, 95% 0.1% formic acid in water/ 5% 0.1% formic acid in acetonitrile. Flash chromatography was performed on silica gel (230 – 400 Mesh, Grade 60) under a positive pressure of air.

Experimental

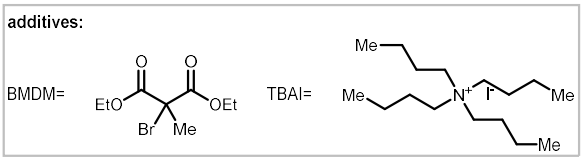
Data Visualization: Analytical Studio Pro from Virscidian (version 10.8) was used to process the UPLC data files in total wavelength chromatogram (TWC), and to generate machine-readable reports in .csv files. Code for chemoinformatics and visualization was written in Python (version 3.9.7). All Python dependencies were installed using Conda version 4.10.3, via Miniforge's arm64 distribution. Matplotlib (version 3.4.3) and Seaborn (version 0.11.2) were both used to create plots and graphs. Pandas (1.3.4) was used to parse excel files and other data formats.

General Optimization Procedure for Benzylic Katritzky Salts: In an inert atmosphere glovebox, either potassium carboxylate salt (0.12 mmol, 1.2 equiv) or free carboxylic acid (0.12 mmol, 1.2 equiv) and associated base (0.12 mmol, 1.2 equiv) were weighed into a dry 2-dram vial. 1 mL of solvent was added, and the mixture stirred for 5 minutes. Following this, Katritzky salt (0.1 mmol, 1 equiv) and additive (1 equiv or 0.2 equiv) were added. The vial was capped, removed from the glovebox, and heated at 80 °C with stirring for 22 hours. Upon completion, 1.00 mL of a 0.033 M trimethoxybenzene solution in ethyl acetate (EtOAc) was added to the reaction mixture. This was further diluted with 3 mL of EtOAc and partitioned between 10 mL of EtOAc and 10 mL of saturated sodium sulfate. Additional EtOAc (10 mL/0.1 mmol acid) and saturated aqueous sodium sulfate (10 mL / 0.1 mmol acid) was added. The aqueous layer was extracted twice more with EtOAc (10 mL / 0.1mmol). The organic layers were combined, dried over sodium sulfate and the solvent removed *in vacuo*. The crude material was then redissolved in chloroform-d and the NMR yield calculated.

Table S1. Extended Optimization Table



entry	base	additive	solvent	% NMR yield
1	R-CO_2K	BMDM	DMF	74
2	KO^{t}Bu	BMDM	DMF	74
3[a]	KO^{t}Bu	BMDM	MeCN	72
4[a]	KO^{t}Bu	BMDM	DMSO	66
5[a]	KO^{t}Bu	BMDM	Cyrene	61
6	R-CO_2K	TBAI	DMF	72
7[b]	KO^{t}Bu	BMDM	DMF	55
8[a,c]	KO^{t}Bu	BMDM	DMF	72

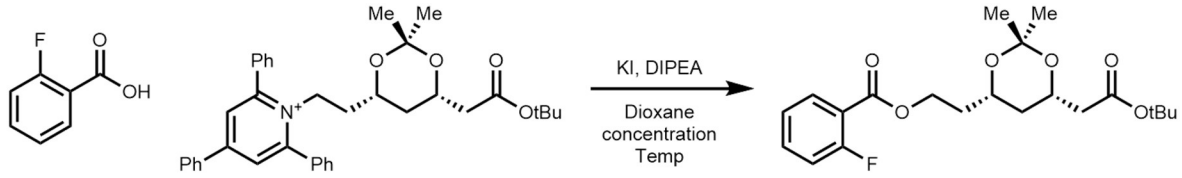


a = 0.2 eq additive
b = under air
c= in the dark

General Optimization Procedure for non-benzylic Katritzky Salts[1]**:** In an inert atmosphere glovebox, carboxylic acid (1.2 mmol, 10 equiv) and Katritzky salt (1.2 mmol, 10 equiv) were weighed into a dry 2-dram vial. 3.78 mL of dioxane and 210 µL (1.2 mmol, 10 equiv) of diisopropylethylamine was added, and the mixture stirred for 5 minutes. 270 µL (1 equiv) of this solution was added to a vial containing 30 µL dioxane, 16 mg (0.1 mmol, 1 equiv) KI, and an additive if present. The reaction was heated for the designated time for 22 hours and cooled to room temperature. After this, internal standard (4.1 µL of benzotrifluoride 0.033 mmol, 0.33 equiv) was added to reach reaction and stirred for 5 minutes, and a 30 µL aliquot dissolved in 570 µL of $CDCl_3$. ^{19}F NMR was performed and the yield calculated.

For the reaction in the dark, the vial was wrapped in tin foil. For the reaction in light, a CFL bulb was shined onto the reaction from six inches away. For the 0.25 M reaction, 130 µL of dioxane was in the vial instead of 30. For the 0.4M reaction the dioxane was not added. For the reaction under air, a needle was poked in the septum.

Table S2. Extended Optimization Table for Primary Amines



Entry	Concentration	Temperature	Additive	% NMR Yield (isolated)
1	0.3M	110 °C	none	82% (78%)
2	0.3M	110 °C	Light	80%
3	0.3M	110 °C	Dark	77%
4	0.3M	120 °C	none	77%
5	0.3M	95 °C	none	82%
6	0.3M	110 °C	Air	69%
7	0.3M	110 °C	H_2O 2 eq	65%
8	0.4 M	110 °C	none	70%
9	0.25 M	110 °C	none	67%
10	0.3M	110 °C	2 equiv KI	81%
11	0.3M	110 °C	0.5 equiv KI	45%

General Procedure A: Carboxylic acid (1 equiv), Katritzky salt (1 equiv), and potassium iodide (1 equiv) were added to an oven dried vial containing a stir bar. The vial was then capped, evacuated, and refilled with N_2 three times. Dioxane (0.3 mL/0.1 mmol acid) was added through the septum to produce a 0.33 M solution. To this solution diisopropylethylamine (DIPEA) (1 equiv, 17.4 µL/ 0.1 mmol acid) was added via syringe, the cap wrapped with parafilm, and heated to the indicated temperature for 22 hours. Following this, the reaction was diluted with

EtOAc (2.5 mL/0.1 mmol acid) and partitioned between additional EtOAc (10 mL/0.1 mmol acid) and saturated aqueous sodium sulfate (10 mL/ 0.1 mmol acid). The aqueous layer was extracted twice more with EtOAc (10 mL / 0.1 mmol). The organic layers were combined, dried over sodium sulfate and the solvent removed *in vacuo*. Purification was achieved as described.

General Procedure B: Carboxylic acid (1.2 equiv) and potassium *tert*-butoxide (KO^tBu) (1.2 equiv) were added to a dried vial and dissolved in 1 mL of dimethylformamide (DMF). This was stirred at room temperature for five minutes followed by the addition of Katritzky salt (1.0 equiv) and 2-bromo-2-methyl diethylmalonate (BMDM) (0.2 equiv, 3.8 µL/0.1 mmol) via syringe. The vial was degassed with N_2 and heated to 80 °C for 22 hours. Following this, the reaction was diluted with EtOAc (2.5 mL/0.1mmol acid) and partitioned between additional EtOAc (10 mL/0.1 mmol acid) and saturated aqueous sodium sulfate (10 mL/ 0.1mmol acid). The aqueous layer was extracted twice more with EtOAc (10 mL / 0.1mmol). The organic layers were combined, dried over sodium sulfate and the solvent removed *in vacuo*. Purification was achieved as described.

General Procedure C (in situ): To an oven-dried vial was added 0.2 mmol of amine, followed by 0.2 mmol of carboxylic acid and 0.2 mmol (32 mg) of potassium iodide. The vial was then capped, evacuated, and refilled with N_2 three times. Dioxane (0.6 mL) was added through the septum via syringe to produce a 0.33 M solution followed by 35 µL of DIPEA. This solution was stirred at room temperature for 5 minutes followed by addition of 0.2 mmol (79 mg) of triphenylpyrylium tetrafluoroborate under a positive pressure of nitrogen. The cap was replaced, wrapped with parafilm, and heated to 110 °C for 22 hours. Following this, the reaction was diluted with EtOAc (5 mL) partitioned between additional EtOAc (20 mL) and saturated aqueous sodium sulfate (20 mL). The aqueous layer was extracted twice more with EtOAc (20 mL). The organic layers were combined, dried over sodium sulfate and the solvent removed *in vacuo*. Purification was achieved as described.

General Procedure for Automation-Assisted Library Synthesis and Analysis

Katritzky salt **45** (790 mg) and potassium iodide (239 mg) were weighed into oven-dried glass vials (ChemGlass #CG-4912-02). 4.8 mL and 3.33 mL of diglyme were added to the Katritzky salt and potassium iodide respectively to make two 0.3 M solutions. Acids were weighed out into individual glass shell vials (Analytical Sales & Services #84001) and loaded onto an empty 96-well tray (Analytical Sales & Services #884001). The weighed masses were submitted to Phactor™, our HTE web application, where the appropriate solvent volumes to generate a 0.3 M stock solution was calculated for each microvial, and then imported into the setup script substrate_screen_solvent_katsalt_KI.py. One parylene-coated stir dowel (Analytical Sales & Services # 13258) was added to each well, and the setup was brought into the glovebox along with the solutions of Katritzky salt and potassium iodide, a 96-well aluminum microvial plate (Analytical Sales & Services # 96973) loaded with empty glass shell vials, diglyme, DIPEA and a deep well reservoir (Analytical Sales & Services # 962144). The Katritzky salt and potassium iodide solutions were placed on a 24-well stirring block (Analytical Sales & Services #24125) mounted on a tumble stirrer (V&P Scientific Inc. 710D3) fitted with a SLAS footprint adaptor (V&P Scientific Inc. 710D3-2), and deck adapter (V&P Scientific Inc. 581B). The glovebox circulation was turned off, and the setup script was loaded into the Opentrons app. The two microvial plates, deep well reservoir and tumble stirrer were mounted on the Opentrons deck as directed by the protocol. 40 mL of a 0.3 M solution of DIPEA in diglyme (prepared by mixing 3.66 mL DIPEA in 66.34 mL diglyme) was prepared and added to the deep well reservoir. The

setup script was subsequently executed, which directs the OT-2 robot to dose appropriate amounts of solvent to each microvial using a single-channel 300 µL pipette (Opentrons P300 Gen 1 Single) fitted with the recommended pipette tips (Opentrons PT0300-9B-NS). The protocol was paused, the tumble stirrer activated to suspend the potassium iodide and Katritzky salt in solution, then the protocol resumed to dose 33 µL of each solution to the blank microvial plate. The Katritzky salt was dosed with Opentrons pipette tips, while potassium iodide was dosed with large orifice tips (USA Scientific 1011-8000). Next, the script substrate_screen_acids.py was executed to transfer each acid solution into the corresponding microwell on the plate containing Katritzky salt and potassium iodide, using an 8-channel pipette (Opentrons P300 Gen 1 Multi) with wide orifice tips. The robot was programmed to pre-mix each solution with 3 repetitions of 100 µL each. The microvial plate was sealed with two layers of rubber mat (Analytical Sales & Services # 96965) and one layer of PFA film (Analytical Sales & Services # 96979), removed from the glovebox, and heated using a heating block (V&P Scientific Inc. 741GA) at 110 °C for 22 hours stirring at 500 RPM (V&P Scientific Inc. 710E5X).

After the reaction time has elapsed, the microvial plate was returned to the robot deck along with a polypropylene 96-well deep well plate (Analytical Sales & Services # 17P687Z) and a fresh deep well reservoir containing 0.1 M caffeine solution in acetonitrile in one well, and Optima grade acetonitrile in the other. Protocol substrate_screen_quench.py was then executed using the 8-channel pipette to first transfer 100 µL of the caffeine “quench” solution into the microvial plate, then transfer 40 µL of the quenched reaction to the polypropylene deep well plate, with premixing of 3 repetitions of 100 µL each. Next, 560 µL of acetonitrile was added to each well of the polypropylene deep well plate. Lastly, the plate was sealed with a polypropylene cap mat (Analytical Sales & Services # 96057) and analyzed with UPLC-MS.

In order for users to calibrate the robot while maintaining eye contact with the robot deck containing pipette tips and labware, a video game controller (PDP 049-005-NA) was connected to the computer on which the Opentrons App was installed, and button presses mapped to the required keyboard inputs for calibration (Figure S2) using Antimicro[2] (version 2.23).

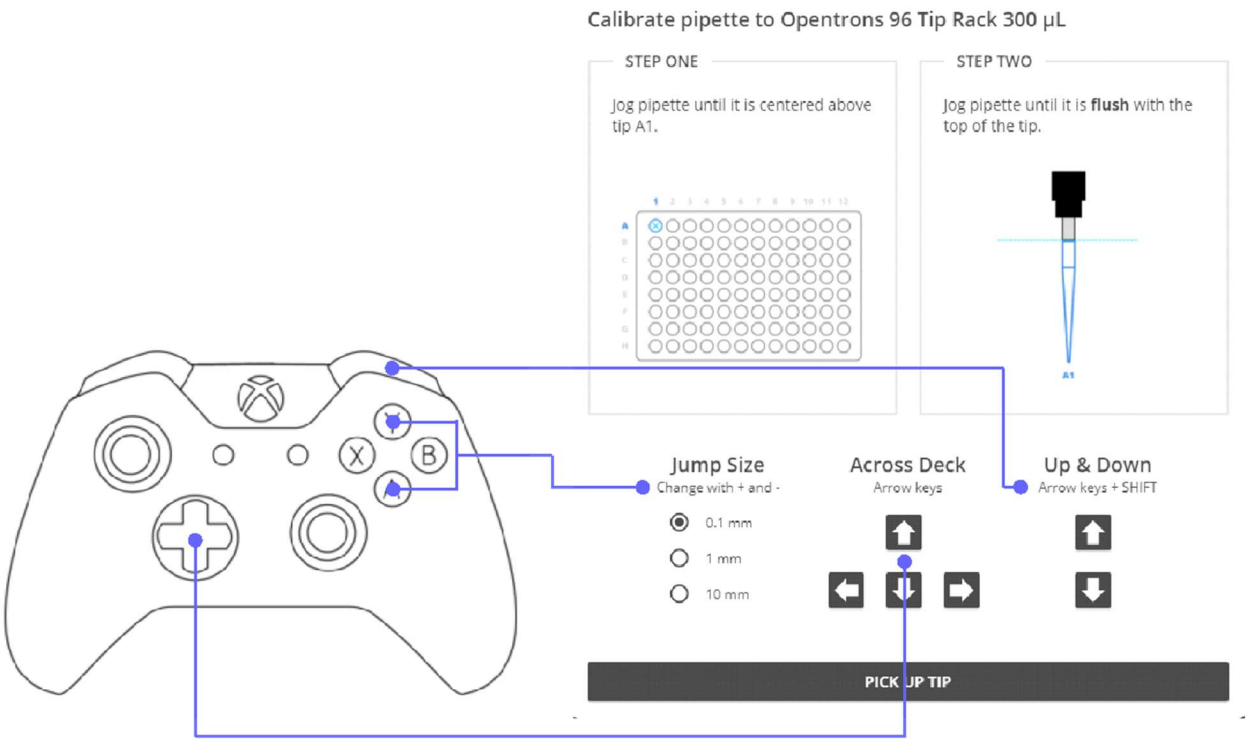
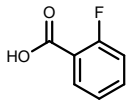


Figure S2. Input mappings for OT-2 robot calibration using a video game controller[2]. The Xbox® controller is pictured, but those of other consoles can also be used as long as they can interface with the driving computer.

Acids used in the screen:



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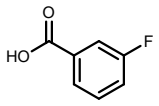

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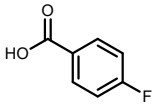

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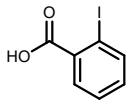

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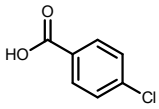

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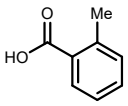

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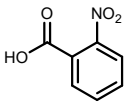

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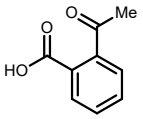

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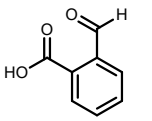

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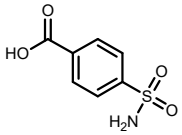

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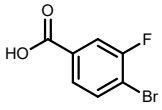

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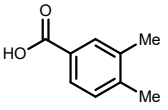

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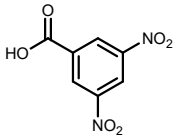

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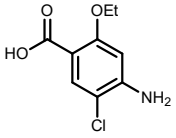

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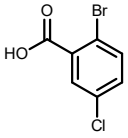

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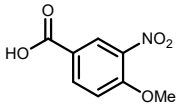

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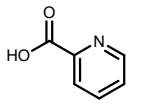

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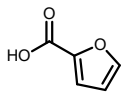

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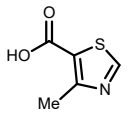

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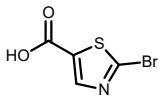

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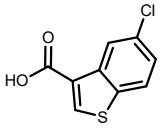

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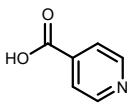

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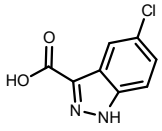

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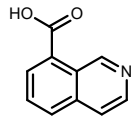

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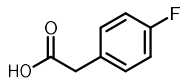

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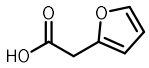

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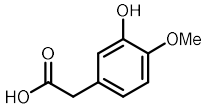

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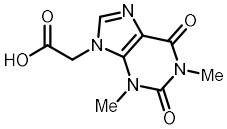

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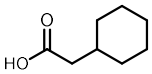

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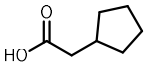

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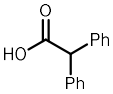

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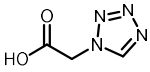

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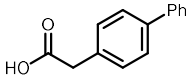

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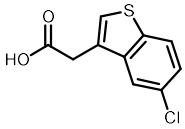

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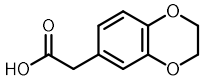

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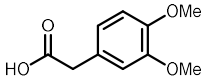

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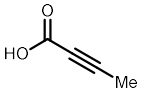

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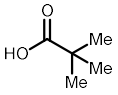

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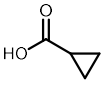

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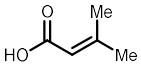

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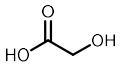

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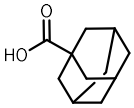

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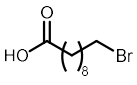

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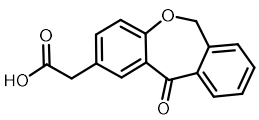

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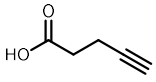

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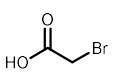

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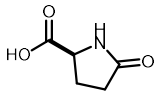

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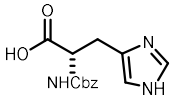

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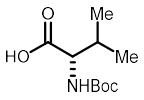

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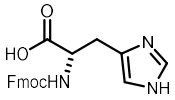

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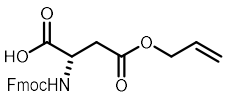

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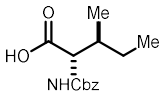

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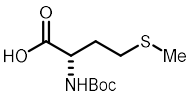

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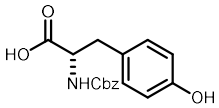

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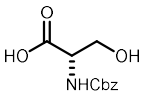

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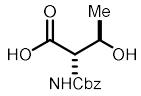

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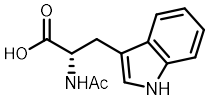

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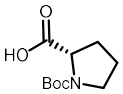

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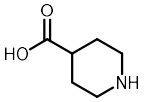

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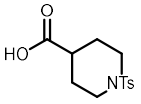

F1

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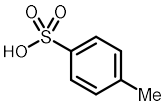

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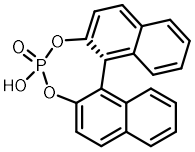

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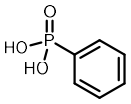

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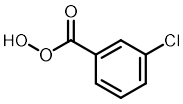

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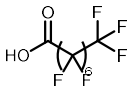

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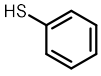

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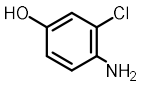

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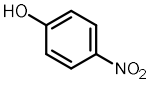

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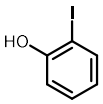

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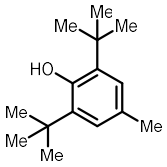

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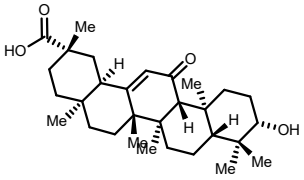

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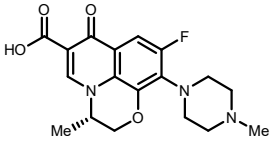

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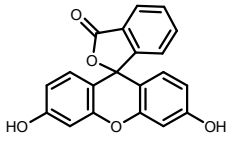

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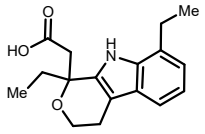

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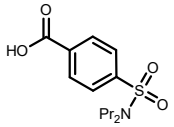

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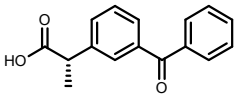

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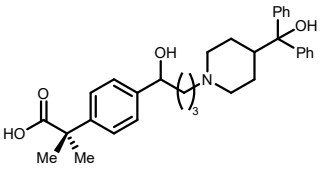

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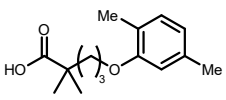

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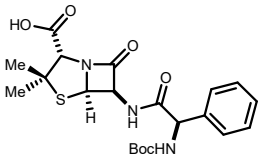
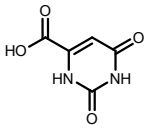
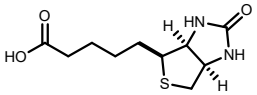


G9



G10



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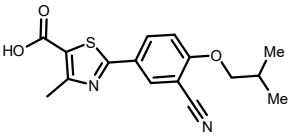

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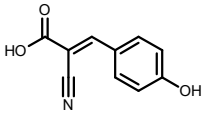

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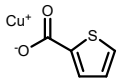
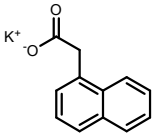


H2



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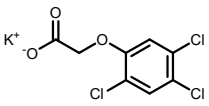

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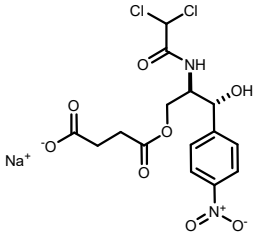

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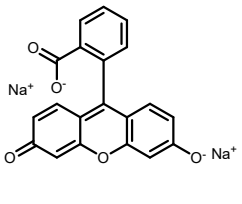
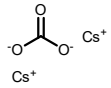
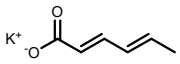


H6

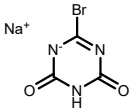
H7



H8

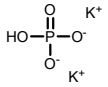


H9



H10

H11



H12

Starting Material Preparation

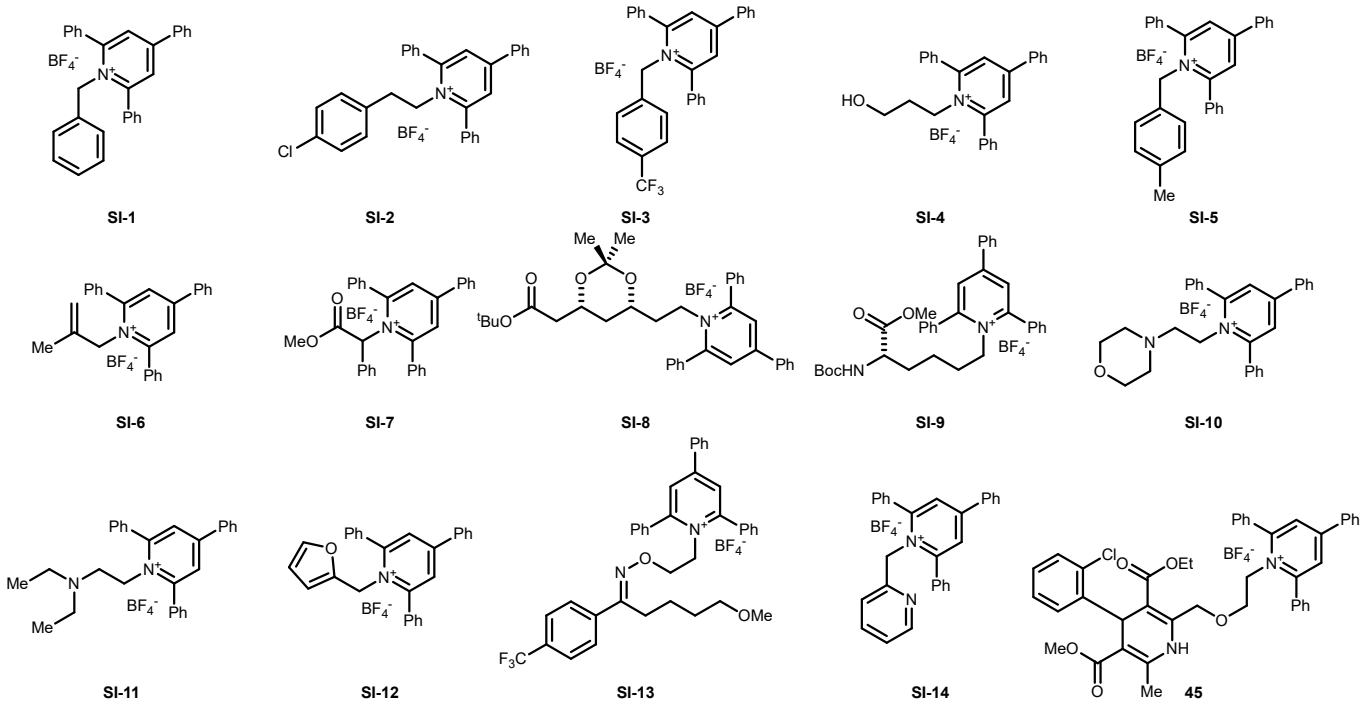
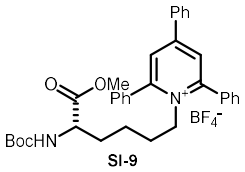


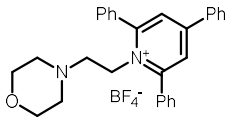
Figure S1. Reported Katritzky Salts

SI-1[4], **SI-2**[5], **SI-3**[4], **SI-4**[6], **SI-5**[4], **SI-6**[7], **SI-7**[8], **SI-8**[9], **SI-11**[10], **SI-12**[11], **SI-14**[11], and **45**[6] were prepared as previously reported. **SI-9**, **SI-10**, and **SI-13** were prepared as described below.



(S)-1-(5-((tert-Butoxycarbonyl)amino)-6-methoxy-6-oxohexyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (SI-9)

Boc-L-lysine methyl ester HCl salt (540 mg, 1.8 mmol, 1.2 equiv) was suspended in ethanol (1.5 mL) followed by the addition of triethylamine (253 µL, 1.8 mmol, 1.2 equiv). This was stirred for 20 minutes followed by the addition of triphenylpyrylium tetrafluoroborate (600 mg, 1.5 mmol, 1.0 equiv). The reaction mixture was heated at 80 °C for four hours. After cooling to room temperature, the reaction mixture was poured into a separatory funnel containing 15 mL of dichloromethane (DCM) and washed with 10 mL of 1 M HCl. The organic layer was collected, dried over sodium sulfate, concentrated *in vacuo* and purified via column chromatography (0→30% acetone in DCM) to give 700 mg (72%) of an off-white solid. Characterization data matches those of the reported compound.[12]



SI-10

1-(2-Morpholinoethyl)-2,4,6-triphenylpyridin-1-ium tetrafluoroborate (SI-10)

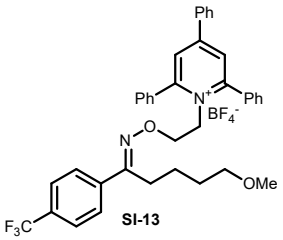
2-morpholinoethan-1-amine (156 mg, 1.2 mmol, 1.2 equiv) was dissolved in 1.0 mL of ethanol followed by the addition of triphenylpyrylium tetrafluoroborate (396 mg, 1.0 mmol, 1.0 equiv). This solution was heated at 80 °C for four hours. Upon cooling to room temperature, the product precipitated and was then filtered, washed with 3×2 mL portions of ethanol, 3×2 mL portions of ether and dried under vacuum overnight to give 340 mg (69%) of product.

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.84 (d, *J* = 4.6 Hz, 6H), 7.76 – 7.71 (m, 2H), 7.62 – 7.57 (m, 6H), 7.56 – 7.46 (m, 3H), 4.66 (t, *J* = 7.4 Hz, 2H), 3.37 (t, *J* = 4.5 Hz, 4H), 2.36 (s, 2H), 1.83 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 156.1, 134.0, 132.9, 132.3, 131.3, 129.8, 129.5, 129.5, 128.3, 126.8, 66.6, 56.9, 53.0, 51.6.

^{19}F NMR (470 MHz, $CDCl_3$) δ −153.0.

HRMS (ESI) Calculated $C_{29}H_{29}N_2O^+$ $[M\text{-}BF_4]^+$: 421.2274, Found 421.2270.



SI-13

(E)-1-(2-(((5-Methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl)-2,4,6-triphenylpyridin-1-ium (SI-13)

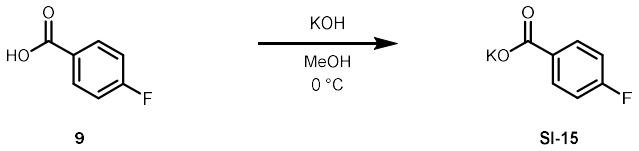
Fluvoxamine maleate (1060 mg, 2.40 mmol, 1.2 equiv) was suspended in 2 mL of ethanol followed by the addition of triethylamine (486 mg, 669 µL, 4.8 mmol, 2.4 equiv). This was stirred for 30 min until homogenous, and followed by the addition of triphenylpyrylium tetrafluoroborate (792 mg, 2.0 mmol, 1.0 equiv). The solution was heated to 80 °C for four hours. Upon cooling to room temperature, the product precipitated and was filtered, washed with 2×2 mL of cold water, 2×2 mL of cold ethanol, and 2×2 mL of diethyl ether. The collected powder was dried under high vacuum to give 1200 mg (86%) of a white solid.

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 6H), 7.67 – 7.61 (m, 2H), 7.61 – 7.54 (m, 6H), 7.54 – 7.44 (m, 5H), 7.37 (d, *J* = 8.2 Hz, 2H), 5.05 (t, *J* = 5.8 Hz, 2H), 4.01 (t, *J* = 5.8 Hz, 2H), 3.24 (d, *J* = 6.5 Hz, 5H), 2.55 (t, *J* = 7.9 Hz, 2H), 1.45 (dt, *J* = 12.0, 6.1 Hz, 2H), 1.37 (ddd, *J* = 15.9, 9.4, 6.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 157.8, 156.2, 138.0, 133.7, 133.1, 132.5, 131.5 (q, J = 32.5 Hz), 131.3, 129.9, 129.6, 129.6, 128.1, 126.6, 126.5, 125.5 (q, J = 3.8 Hz), 125.0 (q, J = 272.9 Hz), 72.1, 70.4, 58.7, 54.6, 29.6, 26.0, 23.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ −62.81, −152.95, −153.01.

HRMS (ESI) Calculated $C_{38}H_{36}F_3N_2O_2^+$ [M-BF_4]$^+$: 609.2723, Found 609.2714.

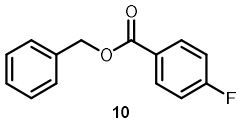


9 SI-15

Potassium 4-fluorobenzoate (SI-15)

SI-15 was prepared by dissolving 2.544 g (18.2 mmol, 1 equiv) of 4-fluorobenzoic acid in 5 mL of methanol within a 25 mL round bottom flask. This solution was cooled in an ice bath with stirring followed by the dropwise addition of a 4 M solution of methanolic KOH (4.50 mL, 18 mmol). The slurry was stirred at 0 °C for one hour, filtered, and vacuum dried overnight to give 2.879 g (89%) of the desired salt.

Characterization



10

Benzyl 4-fluorobenzoate (10)

Ester **10** was prepared on a 0.2 mmol scale from 4-fluorobenzoic acid and **SI-1** at 80 °C via general procedure B to give 36 mg (76%) of a clear oil after purification with EtOAc/hexanes.

Note: Product has an identical R_f to triphenylpyridine in all attempted solvent systems. To remedy this, before loading onto the column, the crude material was taken up in 0.3 mL of EtOAc 30 µL of TFA was added. The product was then eluted with 15% EtOAc in hexanes.

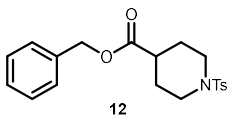
R_f 0.60 in 7:93 EtOAc:hexanes.

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.13 – 8.06 (m, 2H), 7.47 – 7.42 (m, 2H), 7.42 – 7.32 (m, 3H), 7.11 (t, *J* = 8.6 Hz, 2H), 5.36 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.1 (d, *J* = 172.0 Hz), 165.0, 136.1, 132.3 (d, *J* = 9.2 Hz), 128.8, 128.5, 128.4, 126.6, 115.5 (d, *J* = 22.0 Hz), 67.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ −105.6 (tt, *J* = 8.4, 5.1 Hz).

HRMS (ESI) Calculated $C_{14}H_{12}FO_2^+$ [M+H]$^+$: 231.0816, Found 231.0742.



12

Benzyl 1-tosylpiperidine-4-carboxylate (12)

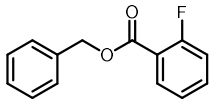
Ester **12** was prepared on a 0.2 mmol scale from N-tosylisonipecotic acid[13] and **SI-1** at 80 °C via general procedure A to give 68 mg (91%) of a white solid after purification with EtOAc/hexanes.

R_f: 0.40 in 20:80 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.38 – 7.26 (m, 7H), 5.09 (s, 2H), 3.61 (dt, *J* = 11.5, 4.1 Hz, 2H), 2.50 – 2.41 (m, 5H), 2.30 (tt, *J* = 10.6, 4.0 Hz, 1H), 2.02 – 1.95 (m, 2H), 1.83 (dtd, *J* = 14.4, 10.8, 4.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 143.7, 135.8, 133.2, 129.8, 128.7, 128.4, 128.1, 127.8, 66.5, 45.5, 40.2, 27.5, 21.6.

HRMS (ESI) Calculated $C_{20}H_{24}NO_4S^+$ $[M+H]^+$: 374.1421, Found 374.1414.



13

Benzyl 2-fluorobenzoate (13)

Ester **13** was prepared on a 0.2 mmol scale from 2-fluorobenzoic acid and **SI-1** at 80 °C via general procedure B to give 33 mg (72%) of a clear oil after purification with diethyl ether/hexanes.

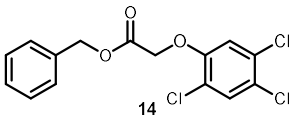
R_f 0.70 in 7:93 Et_2O:hexanes.

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 1H), 7.55 – 7.50 (m, 1H), 7.50 – 7.44 (m, 2H), 7.44 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 7.21 (ddt, *J* = 8.9, 6.4, 1.2 Hz, 1H), 7.15 (ddd, *J* = 10.9, 8.3, 1.4 Hz, 1H), 5.40 (d, *J* = 2.1 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (d, *J* = 3.7 Hz), 162.1 (d, *J* = 260.4 Hz), 135.9, 134.6 (d, *J* = 9.1 Hz), 132.3, 128.7, 128.4, 128.2, 124.0 (d, *J* = 3.9 Hz), 118.7 (d, *J* = 9.5 Hz), 117.0 (d, *J* = 22.4 Hz), 67.0.

^{19}F NMR (470 MHz, $CDCl_3$) δ −108.9– −109.2 (m).

HRMS (ESI) Calculated $C_{14}H_{12}FO_2^+$ $[M+H]^+$: 231.0816, Found 231.0764.



14

Benzyl 2-(2,4,5-trichlorophenoxy)acetate (14)

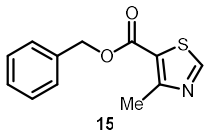
Ester **14** was prepared on a 0.2 mmol scale from commercially available potassium 2,4,5-trichlorophenoxyacetate and **SI-1** at 80 °C via a modified procedure A where base was excluded to give 53 mg (76%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.54 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.47 (d, *J* = 0.8 Hz, 1H), 7.41 – 7.31 (m, 5H), 6.89 (s, 1H), 5.25 (s, 2H), 4.72 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 152.7, 135.0, 131.4, 131.3, 128.8, 128.6, 125.7, 122.8, 115.7, 67.5, 66.6.

HRMS (ESI) Calculated $C_{15}H_{12}Cl_3O_3^+$ $[M+H]^+$: 344.9847, Found 344.9832.



15

Benzyl 4-methylthiazole-5-carboxylate (15)

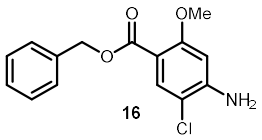
Ester **15** was prepared on a 0.2 mmol scale from 4-methylthiazole-5-carboxylic acid and **SI-1** at 80 °C via general procedure A to give 33 mg (70%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.26 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.78 (s, 1H), 7.45 – 7.33 (m, 5H), 5.33 (s, 2H), 2.78 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9, 161.1, 155.4, 135.5, 128.7, 128.4, 128.2, 128.2, 67.0, 17.4.

HRMS (ESI) Calculated $C_{12}H_{12}NO_2S^+$ $[M+H]^+$: 234.0583, Found 234.0587.



16

Benzyl 4-amino-5-chloro-2-methoxybenzoate (16)

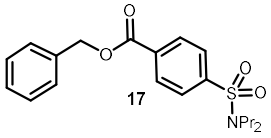
Ester **16** was prepared on a 0.1 mmol scale from 4-amino-5-chloro-2-methoxy benzoic acid and **SI-1** at 80 °C via general procedure B to give 19 mg (64%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.45 in 50:50 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.30 (m, 3H), 6.30 (s, 1H), 5.29 (s, 2H), 3.84 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5, 160.6, 147.9, 136.6, 133.5, 128.6, 128.2, 128.1, 110.2, 109.8, 98.5, 66.2, 56.2.

HRMS (ESI) Calculated $C_{15}H_{15}ClNO_3^+$ $[M+H]^+$: 292.0735, Found 292.0729.



17

Benzyl 4-(N,N-dipropylsulfamoyl)benzoate (17)

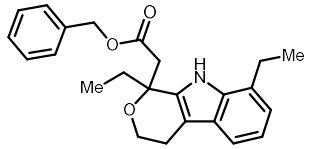
Ester **17** was prepared on a 0.1 mmol scale from probenecid and **SI-1** at 80 °C via general procedure B to give 24 mg (64%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.41 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.48 – 7.33 (m, 4H), 5.39 (s, 2H), 3.09 (t, *J* = 7.5 Hz, 4H), 1.54 (h, *J* = 7.4 Hz, 4H), 0.86 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 144.4, 135.5, 133.4, 130.3, 128.7, 128.5, 128.4, 127.0, 67.3, 49.9, 21.9, 11.1.

HRMS (ESI) Calculated $C_{20}H_{26}NO_4S^+$ $[M+H]^+$: 376.1577, Found 376.1570.



18

Benzyl 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetate (18)

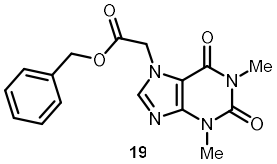
Ester **18** was prepared on a 0.2 mmol scale from etodolac and **SI-1** at 80 °C via general procedure A to give 55 mg (74%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.46 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.99 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.10 – 7.03 (m, 1H), 7.01 (dt, *J* = 7.2, 1.0 Hz, 1H), 5.21 – 5.10 (m, 2H), 4.08 – 4.00 (m, 1H), 3.98 – 3.89 (m, 1H), 3.07 (d, *J* = 16.5 Hz, 1H), 2.97 (d, *J* = 16.6 Hz, 1H), 2.90 – 2.82 (m, 2H), 2.84 – 2.78 (m, 1H), 2.74 (dt, *J* = 15.2, 4.5 Hz, 1H), 2.16 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.01 (dq, *J* = 14.0, 7.3, 6.8 Hz, 1H), 1.55 (s, 1H), 1.36 (td, *J* = 7.6, 0.9 Hz, 3H), 0.83 (td, *J* = 7.4, 0.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 135.9, 135.4, 128.6, 128.4, 128.2, 126.6, 126.2, 120.4, 119.6, 115.9, 108.5, 74.6, 66.8, 60.6, 43.1, 30.7, 24.2, 22.4, 13.7, 7.6.

HRMS (ESI) Calculated $C_{24}H_{28}NO_3^+$ $[M+H]^+$: 378.2064, Found 378.2067.



19

Benzyl 2-(1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydro-7H-purin-7-yl)acetate (19)

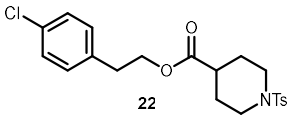
Ester **19** was prepared on a 0.35 mmol scale from theophylline-7-acetic acid and **SI-1** at 80 °C via general procedure A to give 102 mg (89%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.38 in 100% EtOAc

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.36 (dd, *J* = 3.1, 1.1 Hz, 5H), 5.24 (s, 2H), 5.13 (s, 2H), 3.60 (s, 3H), 3.38 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 155.4, 151.8, 148.6, 141.9, 134.8, 128.9, 128.8, 128.7, 107.3, 68.2, 47.5, 30.0, 28.1.

HRMS (ESI) Calculated $C_{16}H_{17}N_4O_4^+$ $[M+H]^+$: 329.1244, Found 329.1235.



22

4-Chlorophenethyl 1-tosylpiperidine-4-carboxylate (22)

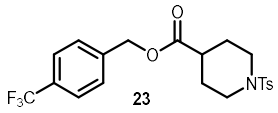
Ester **22** was prepared on a 0.2 mmol scale from N-tosylisonipecotic acid and **SI-2** at 110 °C via general procedure A to give 49 mg (58%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.28 in 25:75 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.13 – 7.06 (m, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.58 (dt, *J* = 12.1, 4.1 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 2.43 (dd, *J* = 22.8, 3.0 Hz, 2H), 2.43 (s, 3H), 2.20 (tt, *J* = 10.6, 4.0 Hz, 1H), 1.95 – 1.85 (m, 2H), 1.75 (dtd, *J* = 14.3, 10.7, 3.9 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 143.7, 136.2, 133.2, 132.6, 130.3, 129.8, 128.7, 127.8, 64.8, 45.5, 40.1, 34.5, 27.5, 21.6.

HRMS (ESI) Calculated $C_{21}H_{25}ClNO_4S^+$ $[M+H]^+$: 422.1187, Found 422.1181.



23

4-(Trifluoromethyl)benzyl 1-tosylpiperidine-4-carboxylate (23)

Ester **23** was prepared on a 0.2 mmol scale from N-tosylisonipecotic acid and **SI-3** at 110 °C via general procedure A to give 76 mg (86%) of a white solid after purification with EtOAc/hexanes.

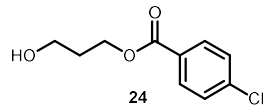
R_f = 0.31 in 20:80 EtOAc:Hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.57 (m, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 2H), 3.64 (dt, *J* = 12.3, 4.0 Hz, 2H), 2.51 – 2.40 (m, 5H), 2.32 (tt, *J* = 10.7, 4.0 Hz, 1H), 2.00 (dd, *J* = 13.7, 3.8 Hz, 2H), 1.84 (dtd, *J* = 14.4, 10.8, 4.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.59, 143.77, 139.86, 133.31, 130.64 (q, *J* = 32.6 Hz), 129.82, 128.16, 127.82, 125.66 (q, *J* = 3.8 Hz), 123.00 (q, *J* = 268.4 Hz), 65.59, 45.48, 40.22, 27.58, 21.65.

^{19}F NMR (376 MHz, $CDCl_3$) δ −62.67.

HRMS (ESI) Calculated $C_{21}H_{23}F_3NO_4S^+$ $[M+H]^+$: 442.1294, Found 442.1290.



24

3-Hydroxypropyl 4-chlorobenzoate (24)

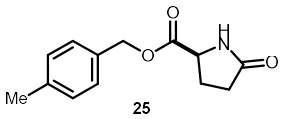
Ester **24** was prepared on a 0.1 mmol scale from p-chlorobenzoic acid and **SI-4** at 110 °C via general procedure A to give 18 mg (82%) of a yellow oil after purification with EtOAc/hexanes.

R_f = 0.16 in 25:75 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.7, 2.0 Hz, 2H), 7.40 (dt, *J* = 9.1, 2.2 Hz, 2H), 4.47 (td, *J* = 6.2, 1.8 Hz, 2H), 3.76 (td, *J* = 6.1, 1.4 Hz, 2H), 2.12 (s, 1H), 2.00 (pd, *J* = 6.1, 1.3 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 139.6, 131.1, 128.9, 128.7, 62.2, 59.2, 32.0.

HRMS (ESI) Calculated $C_{10}H_{12}ClO_3^+$ $[M+H]^+$: 215.0469, Found 215.0448.



25

4-Methylbenzyl (*S*)-5-oxopyrrolidine-2-carboxylate (25)

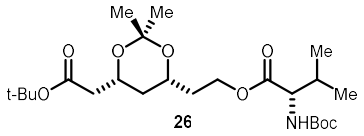
Ester **25** was prepared on a 0.2 mmol scale from pyroglutamic acid and **SI-5** at 80 °C via general procedure A to give 44 mg (94%) of a white solid after purification with EtOAc/hexanes.

R_f: 0.34 in 100% EtOAc

^{1}H NMR (499 MHz, CDCl3) δ 7.23 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.89 (s, 1H), 5.13 (s, 2H), 4.24 (dd, J = 8.5, 4.9 Hz, 1H), 2.45 – 2.24 (m, 6H), 2.22 – 2.12 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.2, 172.0, 138.5, 132.2, 129.4, 128.6, 67.3, 55.6, 29.3, 24.8, 21.2..

HRMS (ESI) Calculated $C_{13}H_{16}NO_3^+$ $[M+H]^+$: 234.1125, Found 234.1126.



26

2-((4*R*,6*R*)-6-(2-(tert-Butoxy)-2-oxoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl (*tert*-butoxycarbonyl)-*L*-valinate (26)

Ester **26** was prepared on a 0.2 mmol scale from N-Boc-*L*-valine and **SI-8** at 110 °C via general procedure A to give 65 mg (69%) of a clear oil after purification with EtOAc/hexanes.

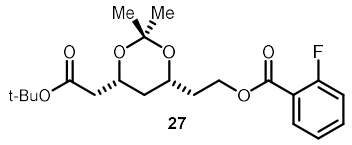
R_f = 0.33 in 15:85 EtOAc:Hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 5.02 (d, *J* = 9.1 Hz, 1H), 4.29 – 4.16 (m, 4H), 3.97 (dtd, *J* = 11.7, 6.3, 5.6, 2.4 Hz, 1H), 2.42 (dd, *J* = 15.2, 7.1 Hz, 1H), 2.29 (dd, *J* = 15.1, 6.1 Hz, 1H), 2.11 (dq, *J*

= 13.1, 6.8 Hz, 1H), 1.81 – 1.74 (m, 2H), 1.56 (dt, *J* = 12.7, 2.4 Hz, 1H), 1.44 (d, *J* = 1.3 Hz, 18H), 1.41 (s, 3H), 1.34 (s, 3H), 1.28 – 1.15 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 158.2, 139.7, 139.0, 131.2, 131.0, 128.9, 128.8, 128.7, 126.7, 125.6, 125.5, 125.5, 125.5, 72.4, 72.1, 63.8, 58.7, 29.7, 26.4, 23.2.

HRMS (ESI) Calculated $C_{24}H_{43}NNaO_8^+$ $[M+Na]^+$: 496.2881, Found 496.2932.



27

2-((4*R*,6*R*)-6-(2-(*tert*-Butoxy)-2-oxoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)ethyl 2-fluorobenzoate (27)

Ester **27** was prepared on a 0.2 mmol scale from 2-fluorobenzoic acid and **SI-8** at 110 °C via general procedure A to give 61 mg (78%) of a clear oil after purification with EtOAc/hexanes.

Ester **27** was also prepared on a 0.2 mmol scale from 2-fluorobenzoic acid and tert-butyl 2-((4R,6R)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate *in situ* via procedure C to give 44 mg (56%) of a clear oil after purification.

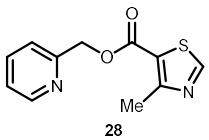
R_f = 0.44 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.89 (td, *J* = 7.6, 1.9 Hz, 1H), 7.48 (dddd, *J* = 8.6, 6.9, 4.7, 1.8 Hz, 1H), 7.18 (t, 1H), 7.10 (dd, *J* = 10.8, 8.3 Hz, 1H), 4.41 (td, *J* = 6.4, 2.5 Hz, 2H), 4.25 (dtd, *J* = 11.6, 6.5, 2.4 Hz, 1H), 4.07 (qd, *J* = 7.5, 2.4 Hz, 1H), 2.41 (dd, *J* = 15.1, 7.0 Hz, 1H), 2.28 (dd, *J* = 15.1, 6.1 Hz, 1H), 1.86 (q, *J* = 6.3 Hz, 2H), 1.59 (dt, *J* = 12.7, 2.5 Hz, 1H), 1.41 (d, *J* = 2.8 Hz, 12H), 1.33 (s, 3H), 1.23 (q, *J* = 11.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.4, 164.6 (d, J = 3.8 Hz), 162.1 (d, J = 259.8 Hz), 134.5 (d, J = 9.0 Hz), 132.2, 124.1 (d, J = 4.1 Hz), 119.1 (d, J = 10.0 Hz), 117.1 (d, J = 22.4 Hz), 99.0, 80.7, 66.4, 65.9, 61.7, 42.8, 36.7, 35.5, 30.2, 28.2, 19.8.

^{19}F NMR (470 MHz, $CDCl_3$) δ −109.4 (tt, *J* = 10.3, 4.9 Hz).

HRMS (ESI) Calculated $C_{21}H_{29}FNaO_6^+$ $[M+Na]^+$: 419.1846, Found 419.1828.



28

Pyridin-2-ylmethyl 4-methylthiazole-5-carboxylate (28)

Ester **28** was prepared on a 5.00 mmol scale from 4-methyl-5-thiazole carboxylic acid and **SI-14** at 110 °C via a modified general procedure A where a 50 mL round bottom flask equipped a

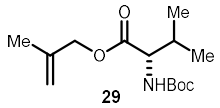
reflux condenser and a septum was used in place of a vial and workup was accomplished with 75 mL of aqueous sodium sulfate and 3×100 mL of EtOAc. 670 mg (61%) of a tan solid was obtained after purification with EtOAc/hexanes.

R_f: 0.50 in 100% EtOAc

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.60 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.72 (td, *J* = 7.7, 1.6 Hz, 1H), 7.40 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.24 (ddd, *J* = 7.6, 4.9, 1.2 Hz, 1H), 5.44 (s, 2H), 2.79 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8, 161.5, 155.7, 155.5, 149.6, 137.0, 123.1, 121.8, 121.7, 67.5, 17.5.

HRMS (ESI) Calculated $C_{11}H_{11}N_2O_2S^+$ $[M+H]^+$: 235.0536, Found 235.0544.



29

2-Methylallyl (*tert*-butoxycarbonyl)-*L*-valinate (29)

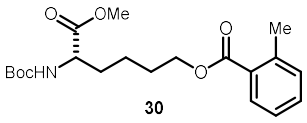
Ester **29** was prepared on a 0.2 mmol scale from N-Boc-*L*-valine and **SI-6** at 80 °C via general procedure A to give 35 mg (64%) of a clear oil after purification with EtOAc/hexanes.

R_f: 0.50 in 15:85 EtOAc:Hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 5.05 – 4.98 (m, 2H), 4.97 – 4.93 (m, 1H), 4.61 – 4.49 (m, 2H), 4.26 (dd, *J* = 9.2, 4.7 Hz, 1H), 2.16 (ddd, *J* = 14.3, 9.9, 6.4 Hz, 1H), 1.76 (d, *J* = 1.4 Hz, 3H), 1.44 (s, 9H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 155.8, 139.6, 113.8, 79.9, 68.5, 58.7, 31.4, 28.4, 19.7, 19.2, 17.6.

HRMS (ESI) Calculated $C_{14}H_{25}NNaO_4^+$ $[M+Na]^+$: 294.1681, Found 294.1672.



30

(*S*)-5-((*tert*-Butoxycarbonyl)amino)-6-methoxy-6-oxohexyl 2-methylbenzoate (30)

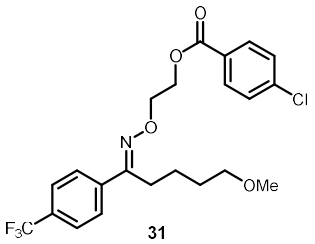
Ester **30** was prepared on a 0.117 mmol scale from o-toluic acid and **SI-9** at 110 °C via general procedure A to give 26 mg (69%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.40 in 25:75 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.38 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 – 7.20 (m, 2H), 5.07 – 5.02 (m, 1H), 4.34 – 4.24 (m, 3H), 3.72 (s, 3H), 2.58 (s, 3H), 1.87 (ddt, *J* = 15.3, 9.9, 6.3 Hz, 1H), 1.83 – 1.73 (m, 2H), 1.73 – 1.63 (m, 1H), 1.57 – 1.44 (m, 2H), 1.43 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 167.8, 155.5, 140.2, 132.0, 131.8, 130.6, 129.9, 125.8, 80.0, 64.4, 53.4, 52.4, 32.6, 28.4, 28.4, 22.1, 21.9.

HRMS (ESI) Calculated $C_{20}H_{29}NNaO_6^+$ $[M+Na]^+$: 402.1893, Found 402.1882.



31

(*E*)-2-(((5-Methoxy-1-(4-(trifluoromethyl)phenyl)pentylidene)amino)oxy)ethyl 4-chlorobenzoate (31)

Ester **31** was prepared on a 0.1 mmol scale from p-chloro benzoic acid and **SI-13** at 110 °C via a modified general procedure A where the solvent was 90/10 v/v dioxane/DMF and two equivalents of potassium iodide (32 mg) were used to give 40 mg (88%) of a white solid after purification with EtOAc/hexanes.

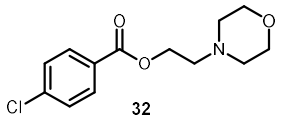
R_f: 0.38 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.36 (m, 2H), 4.65 – 4.59 (m, 2H), 4.54 – 4.48 (m, 2H), 3.27 (d, *J* = 10.2 Hz, 5H), 2.81 – 2.74 (m, 2H), 1.58 (t, *J* = 3.4 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.8, 158.2, 139.7, 139.0, 131.2, 131.0, 128.8, 128.7, 126.7, 125.5 (q, *J* = 3.9 Hz), 125.2 (q, *J* = 270.7 Hz), 72.4, 72.1, 63.8, 58.7, 29.7, 26.4, 23.2.

^{19}F NMR (470 MHz, $CDCl_3$) δ −62.8.

HRMS (ESI) Calculated $C_{22}H_{24}ClF_3NO_4^+$ $[M+H]^+$: 458.1340, Found 458.1371.



32

2-Morpholinoethyl 4-chlorobenzoate (32)

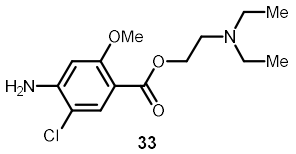
Ester **32** was prepared on a 0.15 mmol scale from p-chlorobenzoic acid and **SI-10** at 110 °C via a modified general procedure A where there was no aqueous work up. Instead, the reaction mixture was concentrated and loaded directly onto a silica gel column to give 31 mg (78%) of a yellow oil after purification with DCM, methanol, and triethylamine.

R_f = 0.38 in 94:5:1 DCM:MeOH:TEA

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.96 (d, *J*=8.5 Hz, 2H), 7.42 (d, *J*=8.5 Hz, 2H), 4.46 (t, *J* = 5.8 Hz, 2H), 3.75 (t, *J*=4.6 Hz, 4H), 2.78 (t, *J* = 5.9 Hz, 2H), 2.58 (t, *J* = 4.7 Hz, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 139.8, 131.2, 129.0, 128.6, 66.6, 62.2, 57.1, 53.8.

HRMS (ESI) Calculated $C_{13}H_{17}ClNO_3^+$ [M+H]$^+$: 270.0891, Found 270.0891.



33

2-(Diethylamino)ethyl 4-amino-5-chloro-2-methoxybenzoate (33)

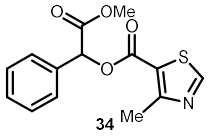
Ester **33** was prepared on 0.2 mmol scale from 4-amino-5-chloro-2-methoxy benzoic acid and **SI-11** at 80 °C via a modified general procedure A where there was no aqueous work up. Instead the reaction mixture was concentrated and loaded directly onto a silica gel column to give 26 mg (44%) of a yellow oil after purification with chloroform/methanol/triethylamine.

R_f: 0.33 in 94:5:1 $CHCl_3$:MeOH:TEA

^{1}H NMR (499 MHz, dmso) δ 7.59 (s, 1H), 6.44 (s, 1H), 6.13 (s, 2H), 4.14 (t, *J* = 5.9 Hz, 2H), 3.71 (s, 3H), 2.71 (s, 2H), 2.55 (s, 4H), 0.97 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (126 MHz, dmso) δ 163.6, 159.8, 149.9, 132.4, 107.8, 97.7, 67.0, 55.5, 50.7, 47.0, 45.7, 25.1.

HRMS (ESI) Calculated $C_{14}H_{22}ClN_2O_3^+$ [M+H]$^+$: 301.1313, Found 301.1304.



34

2-Methoxy-2-oxo-1-phenylethyl 4-methylthiazole-5-carboxylate (34)

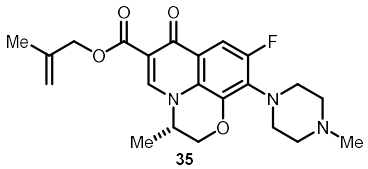
Ester **34** was prepared on a 0.2 mmol scale from 4-methyl-thiazole-5-carboxylic acid and **SI-7** at 80 °C via general procedure A to give 12 mg (21) % of a white solid after purification with EtOAc/ hexanes.

Rf: 0.13 in 15:85 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.56 – 7.50 (m, 2H), 7.45 – 7.40 (m, 3H), 6.13 (s, 1H), 3.76 (s, 3H), 2.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.1, 162.0, 161.4, 156.1, 133.6, 129.6, 129.1, 127.8, 121.4, 75.2, 53.0, 17.7.

HRMS (ESI) Calculated $C_{14}H_{14}NO_4S^+$ [M+H]$^+$: 292.0638, Found 292.0590.



35

2-Methylallyl(*S*)-9-fluoro-3-methyl-10-(4-methylpiperazin-1-yl)-7-oxo-2,3-dihydro-7H-[1,4]oxazino[2,3,4-ij]quinoline-6-carboxylate (35)

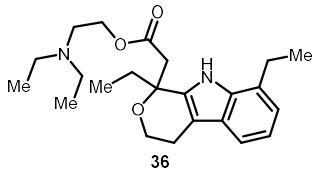
Ester **35** was prepared on a 90 µmol scale from levofloxacin and **SI-6** at 80 °C via a modified general procedure A. After completion of the reaction, one equivalent of KO^{t}Bu (10 mg) was added to the reaction mixture, and all solvent completely removed. The crude mixture was partitioned between 1 mL of EtOAc and 1 mL of water. The aqueous layer was collected and purified by PrepLC on a Teledyne ISCO CombiFlash® EZ Prep (RediSep Prep C18, 100 Å, 5 µm, 150 mm × 20 mm (part no. 692203810), eluent: gradient from 10% MeCN/H_2O to 100% MeCN/H_2O (0 to 2.5 min 10% MeCN. 2.5 to 10 min ramp to 25% hold 5 min. Ramp to 100 % over 7 min. Hold for 3 min. Product came off at 7 min)). Solvent acetonitrile was removed *in vacuo* by a rotary evaporator and water was removed *in vacuo* through lyophilization to give 28 mg (76%) of desired ester.

^{1}H NMR (499 MHz, D_2O) δ 8.36 (s, 1H), 7.42 (d, *J* = 12.6 Hz, 1H), 5.69 – 5.65 (m, 1H), 5.49 – 5.46 (m, 1H), 4.66 – 4.61 (m, 1H), 4.57 – 4.51 (m, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 4.11 (s, 2H), 3.73 (t, *J* = 12.2 Hz, 4H), 3.59 (d, *J* = 9.7 Hz, 4H), 3.25 (s, 3H), 2.06 (s, 3H), 1.51 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (126 MHz, D_2O) δ 174.9, 172.3, 160.3, 156.5, 154.6, 144.1, 140.8 (d, *J* = 6.6 Hz), 132.6, 128.4 (d, *J* = 15.6 Hz), 127.7, 124.6, 123.8, 117.3, 103.4 (d, *J* = 23.8 Hz), 70.8, 68.4, 60.6, 54.6, 46.28, 44.0 (t, *J* = 3.5 Hz), 23.2, 17.1.

^{19}F NMR (470 MHz, D_2O) δ −122.9 (d, *J* = 12.5 Hz).

HRMS (ESI) Calculated $C_{22}H_{27}FN_3O_4^+$ $[M+H]^+$: 416.1980, Found 416.1974.



36

2-(Diethylamino)ethyl 2-(1,8-diethyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-1-yl)acetate (36)

Ester **36** was prepared on a 0.1 mmol scale from etodolac and **SI-11** at 80 °C via general procedure A to give 24 mg (61%) of a white solid after purification with DCM/Methanol/triethylamine.

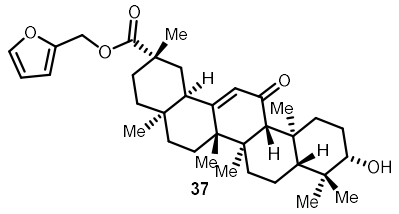
R_f = 0.30 in 5:94:1 MeOH:DCM:TEA

^{1}H NMR (499 MHz, $CDCl_3$) δ 9.09 (s, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.09 – 7.03 (m, 1H), 7.01 (d, *J* = 7.0 Hz, 1H), 4.26 – 4.12 (m, 2H), 4.09 – 4.01 (m, 1H), 3.94 (ddd, *J* = 11.1, 7.3, 4.1 Hz, 1H),

3.03 (d, *J* = 16.6 Hz, 1H), 2.95 (s, 1H), 2.89 (dt, *J* = 15.0, 6.9 Hz, 2H), 2.85 (d, *J* = 0.9 Hz, 1H), 2.79 – 2.72 (m, 1H), 2.68 (t, *J* = 6.7 Hz, 2H), 2.57 (q, *J* = 8.1, 7.7 Hz, 4H), 2.18 (dq, *J* = 14.8, 7.4 Hz, 1H), 2.02 (dq, *J* = 14.0, 7.3, 6.7 Hz, 1H), 1.37 (t, *J* = 8.1 Hz, 3H), 1.02 (t, *J* = 6.6 Hz, 6H), 0.88 – 0.81 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 136.1, 134.6, 126.8, 126.3, 120.5, 119.7, 116.1, 108.5, 74.8, 63.3, 60.8, 51.1, 47.8, 43.2, 30.8, 24.4, 22.6, 13.9, 12.0, 7.7.

HRMS (ESI) Calculated $C_{23}H_{35}N_2O_5^+$ $[M+H]^+$: 387.2642, Found 387.2652.



37

Furan-2-ylmethyl (2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylate (37)

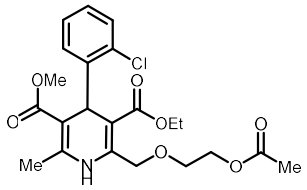
Ester **37** was prepared on a 0.1 mmol scale from18β-Glycyrrhetinic acid and **SI-12** at 60 °C via general procedure A to give 32 mg (61%) of a white solid after purification with EtOAc/hexanes.

R_f = 0.25 in 25:75 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.44 (dd, J = 1.9, 0.8 Hz, 1H), 6.39 (dd, J = 3.3, 0.7 Hz, 1H), 6.35 (dd, J = 3.2, 1.9 Hz, 1H), 5.55 (s, 1H), 5.18 (d, J = 13.0 Hz, 1H), 4.99 (d, J = 13.0 Hz, 1H), 3.21 (dd, J = 11.1, 5.2 Hz, 1H), 2.77 (dt, J = 13.5, 3.6 Hz, 1H), 2.31 (s, 1H), 1.98 (ddd, J = 12.7, 4.3, 1.7 Hz, 3H), 1.89 (ddd, J = 13.6, 4.3, 2.7 Hz, 1H), 1.80 (td, J = 13.6, 4.7 Hz, 1H), 1.68 – 1.56 (m, 6H), 1.48 – 1.29 (m, 3H), 1.33 (s, 3H), 1.29 (d, J = 3.4 Hz, 1H), 1.29 – 1.21 (m, 2H), 1.20 – 1.14 (m, 1H), 1.13 (d, J = 2.2 Hz, 6H), 1.10 (s, 3H), 0.99 (s, 3H), 1.02 – 0.94 (m, 1H), 0.79 (s, 3H), 0.73 (s, 3H), 0.68 (dd, J = 11.8, 1.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 176.1, 169.2, 149.8, 143.4, 128.6, 110.7, 110.6, 78.9, 61.9, 58.0, 55.1, 48.4, 45.5, 44.2, 43.3, 41.2, 39.3, 39.3, 37.7, 37.2, 32.9, 31.9, 31.7, 31.3, 28.6, 28.2, 28.2, 27.4, 26.6, 26.5, 23.4, 18.8, 17.6, 16.5, 15.7.

HRMS (ESI) Calculated $C_{35}H_{51}O_5^+$ $[M+H]^+$: 551.3731, Found 551.3723.



39

3-Ethyl-5-methyl 2-((2-acetoxyethoxy)methyl)-4-(2-chlorophenyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (39)

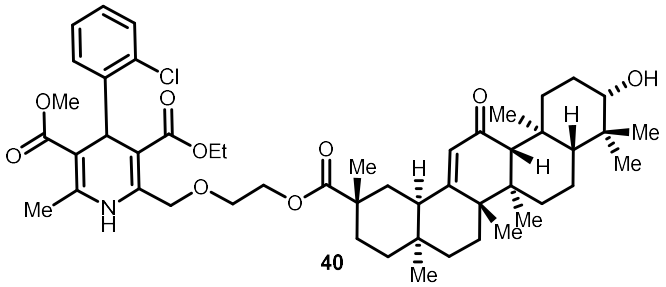
Ester **39** was prepared on a 0.1 mmol scale from acetic acid and **38** at 110 °C via a modified general procedure A where two equivalents of acid (12 mg, 11 µL) and two equivalents of base (26 mg, 35 µL) to give 32 mg (72 %) of a yellow oil after purification with EtOAc/hexanes.

R_f: 0.41 in 40:60 EtOAc:hexanes

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.22 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.12 (ddd, *J* = 7.6, 6.5, 1.4 Hz, 2H), 7.03 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H), 5.40 (s, 1H), 4.78 (dd, *J* = 16.1, 0.7 Hz, 1H), 4.74 – 4.66 (m, 1H), 4.34 (ddd, *J* = 12.2, 5.7, 3.5 Hz, 1H), 4.27 (ddd, *J* = 12.3, 5.3, 3.5 Hz, 1H), 4.05 (dd, *J* = 7.1, 3.0 Hz, 1H), 4.02 (dd, *J* = 7.1, 2.9 Hz, 1H), 3.82 – 3.72 (m, 2H), 3.60 (s, 3H), 2.35 (s, 3H), 2.11 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 168.1, 167.2, 145.8, 145.1, 144.1, 132.4, 131.6, 129.3, 127.5, 127.0, 104.1, 101.6, 69.6, 68.2, 63.3, 59.9, 50.9, 37.2, 21.1, 19.6, 14.4.

HRMS (ESI) Calculated $C_{22}H_{27}ClNO_7^+$ $[M+H]^+$: 452.1471, Found 452.1418.



40

3-Ethyl-5-methyl 4-(2-chlorophenyl)-2-((2-(((2*S*,4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*S*,12b*R*,14b*R*)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carbonyl)oxy)ethoxy)methyl)-6-methyl-1,4-dihydropyridine-3,5-dicarboxylate (40)

Ester **40** was prepared on a 0.1 mmol scale from 18β-Glycyrrhetinic acid and **38** at 110 °C via general procedure A to give 46 mg (52 %) of a yellow oil after purification with EtOAc/hexanes.

R_f: 0.25 in 40:60 EtOAc:hexanes

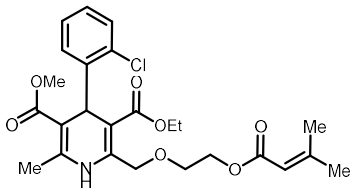
^{1}H NMR (499 MHz, $CDCl_3$) δ 7.35 (ddd, *J* = 7.6, 5.7, 1.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 10.3 Hz, 1H), 7.10 (qd, *J* = 7.5, 1.4 Hz, 1H), 7.03 (tt, *J* = 7.5, 2.1 Hz, 1H), 5.66 (d, *J* = 5.0 Hz, 1H), 5.39 (d, *J* = 2.0 Hz, 1H), 4.77 (dd, *J* = 15.7, 2.1 Hz, 1H), 4.68 (dd, *J* = 15.7, 1.8 Hz, 1H), 4.48 – 4.39 (m, 1H), 4.32 (ddd, *J* = 12.1, 5.4, 3.1 Hz, 1H), 4.04 (ddtt, *J* = 8.7, 7.2, 4.9, 2.3 Hz, 2H), 3.78 (dtdd, *J* = 19.9, 11.1, 6.3, 3.3 Hz, 2H), 3.60 (s, 3H), 3.22 (dd, *J* = 11.0, 5.2 Hz, 1H), 2.79 (dd, *J* = 13.3, 2.2 Hz, 1H), 2.34 (d, *J* = 2.9 Hz, 4H), 2.11 (dd, *J* = 13.5, 4.1 Hz, 1H), 2.02 (ddt, *J* = 13.3, 7.2, 3.5 Hz, 2H), 1.94 (ddd, *J* = 13.6, 4.4, 2.2 Hz, 1H), 1.83 (td, *J* = 13.7, 4.6 Hz, 1H), 1.63 (qd, *J* = 16.2, 14.9, 7.8 Hz, 5H), 1.50 – 1.28 (m, 8H), 1.20 (d, *J* = 12.1 Hz, 1H), 1.20 – 1.14 (m, 6H), 1.17 – 1.11 (m, 7H), 1.07 – 1.00 (m, 1H), 1.00 (s, 3H), 0.96 (dd, *J* = 12.9, 4.4 Hz, 1H), 0.84 – 0.78 (m, 6H), 0.73 – 0.67 (d, *J* = 10.8 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 176.7, 176.7, 169.3, 169.2, 168.2, 167.2, 145.9, 145.9, 144.9, 144.9, 144.3, 144.2, 132.5, 131.6, 129.4, 128.7, 127.5, 127.4, 127.0, 127.0, 104.0, 104.0,

101.8, 101.8, 78.9, 72.1, 70.7, 69.9, 69.8, 68.2, 68.2, 62.9, 62.8, 62.0, 59.9, 59.2, 55.1, 50.9, 48.6, 48.6, 45.5, 44.3, 43.4, 41.3, 39.3, 37.9, 37.3, 37.3, 37.3, 32.9, 32.0, 32.0, 31.4, 28.8, 28.7, 28.7, 28.5, 28.4, 28.2, 27.5, 26.6, 26.6, 26.6, 23.6, 19.6, 19.6, 18.8, 17.6, 16.5, 15.7, 14.4.

^{13}C NMR (126 MHz, $CDCl_3$) δ 200.3, 176.7, 169.3, 168.2, 167.3, 145.9, 144.9, 144.3, 132.5, 131.6, 129.4, 128.7, 127.5, 127.0, 103.9, 101.7, 78.9, 69.9, 68.2, 62.8, 62.0, 61.0, 59.9, 55.1, 50.9, 48.6, 45.5, 44.3, 43.4, 41.3, 39.3, 37.9, 37.3, 32.9, 32.0, 31.3, 28.8, 28.7, 28.5, 28.2, 27.5, 26.6, 26.5, 23.5, 19.6, 18.8, 17.6, 16.5, 15.7, 14.4.

HRMS (ESI) Calculated $C_{50}H_{69}ClNO_9^+$ $[M+H]^+$: 862.4655, Found 862.4556.



41

3-Ethyl-5-methyl 4-(2-chlorophenyl)-6-methyl-2-((2-((3-methylbut-2-enoyl)oxy)ethoxy)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (41)

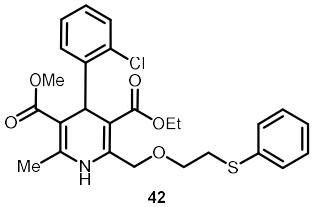
Ester **41** was prepared on a 0.15 mmol scale from 3-methylcrotonic acid and **38** at 110 °C via general procedure A to give 48 mg (64 %) of a clear oil after purification with EtOAc/hexanes.

R_f: 0.62 in 40:60 EtOAc:hexanes

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.18 (s, 1H), 7.14 (td, *J* = 7.5, 1.4 Hz, 1H), 7.05 (td, *J* = 7.6, 1.7 Hz, 1H), 5.74 (p, *J* = 1.4 Hz, 1H), 5.41 (s, 1H), 4.79 (d, *J* = 16.1 Hz, 1H), 4.72 (d, *J* = 16.2 Hz, 1H), 4.36 (dd, *J* = 5.8, 3.5 Hz, 1H), 4.33 (dd, *J* = 5.5, 3.4 Hz, 1H), 4.05 (tq, *J* = 7.1, 3.7 Hz, 2H), 3.79 (ddd, *J* = 5.8, 3.4, 2.3 Hz, 2H), 3.62 (s, 3H), 2.35 (s, 3H), 2.20 (d, *J* = 1.3 Hz, 3H), 1.93 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 167.3, 166.6, 158.2, 145.9, 145.3, 144.2, 132.5, 131.6, 129.4, 127.5, 127.0, 115.6, 104.1, 101.6, 70.0, 68.3, 62.3, 59.9, 50.9, 37.3, 27.6, 20.4, 19.5, 14.4.

HRMS (ESI) Calculated $C_{25}H_{31}ClNO_7^+$ $[M+H]^+$: 492.1784, Found 492.1714.



42

3-Ethyl-5-methyl 4-(2-chlorophenyl)-6-methyl-2-((2-(phenylthio)ethoxy)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (42)

Compound **42** was prepared from thiophenol and **38** on a 0.15 mmol scale at 110 °C via general procedure A to give 66 mg (88 %) of a clear oil after purification with EtOAc/hexanes.

^{1}H NMR (499 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.29 (m, 4H), 7.29 – 7.22 (m, 2H), 7.11 (td, *J* = 7.5, 1.4 Hz, 1H), 7.05 (dd, *J* = 7.7, 1.8 Hz, 1H), 5.41 (s, 1H), 4.78 (d, *J* = 16.2 Hz, 1H), 4.72 (d, *J* = 16.3 Hz, 1H), 4.09 – 4.01 (m, 2H), 3.78 (t, *J* = 5.9 Hz, 2H), 3.62 (s, 3H), 3.21 (td, *J* = 5.9, 2.0 Hz, 2H), 2.32 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 167.3, 145.9, 145.4, 144.2, 135.6, 132.5, 131.6, 129.7, 129.4, 129.3, 127.4, 127.0, 126.8, 104.0, 101.6, 70.0, 68.0, 59.9, 50.9, 37.4, 34.2, 19.7, 19.5, 14.4.

HRMS (ESI) Calculated $C_{26}H_{29}ClNO_5S^+$ $[M+H]^+$: 502.1449, Found 502.1386.

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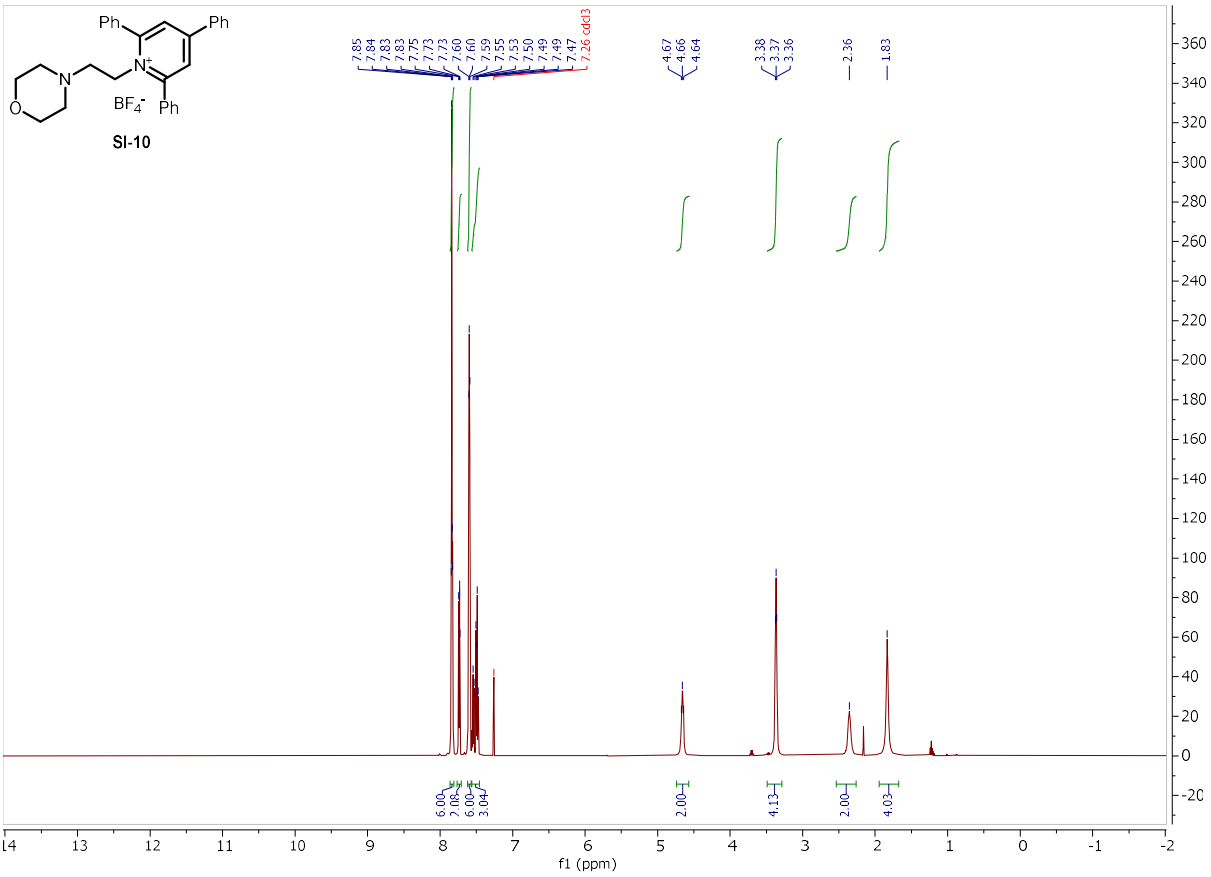

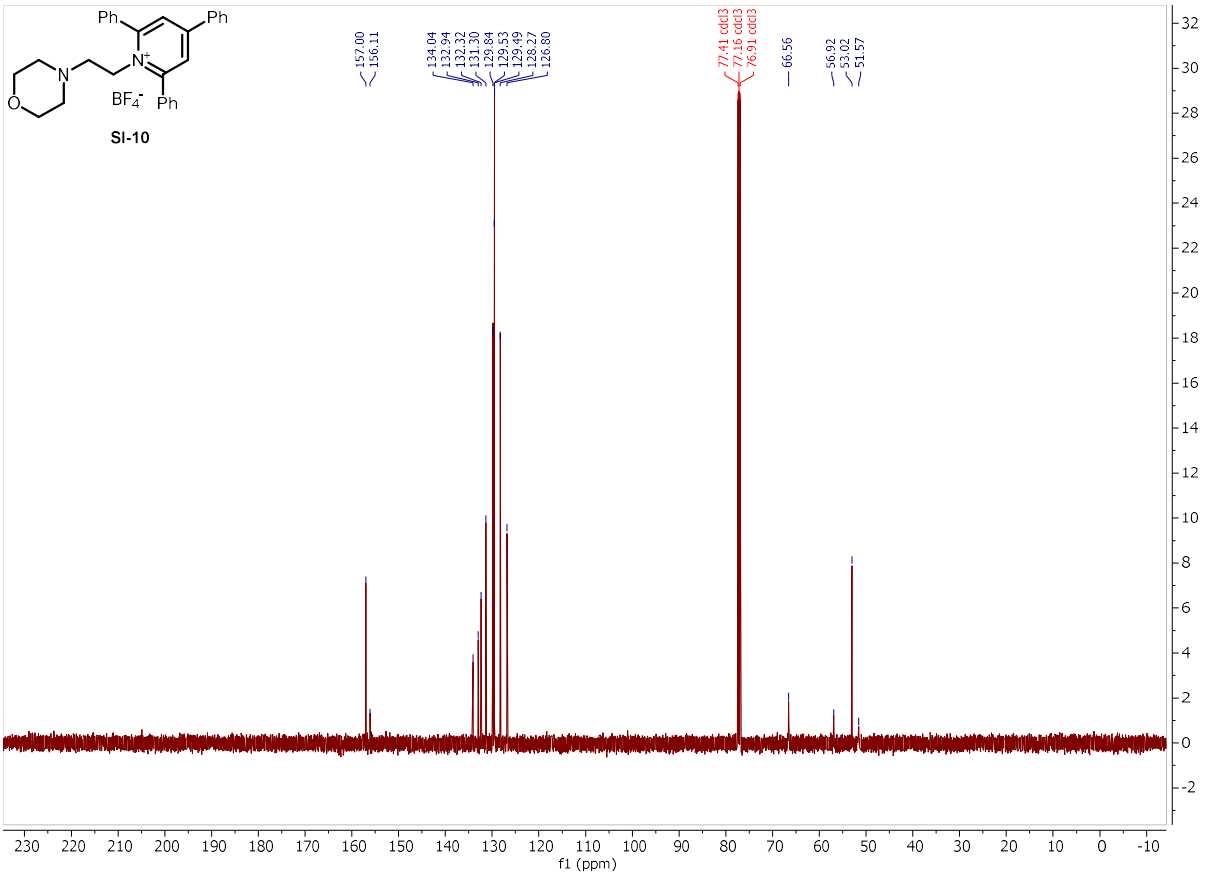
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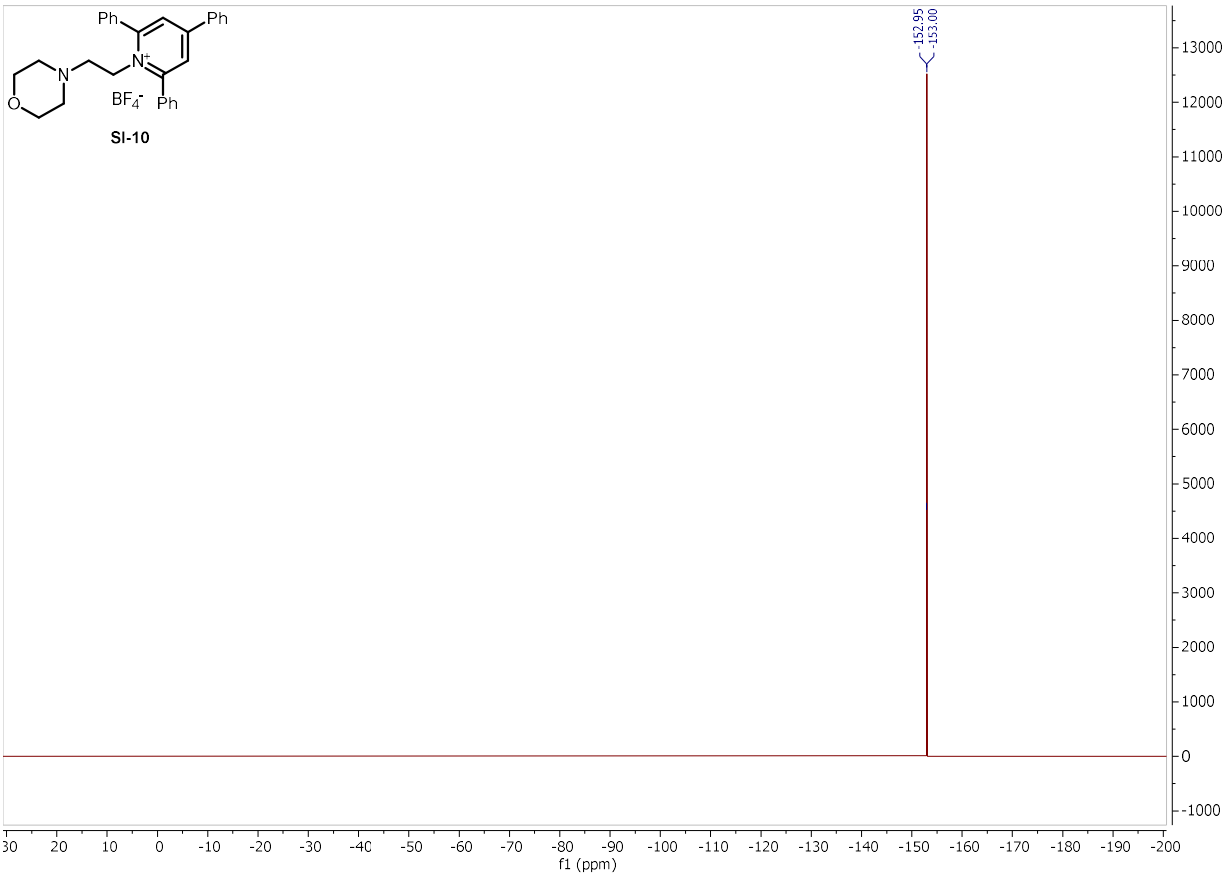
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6000
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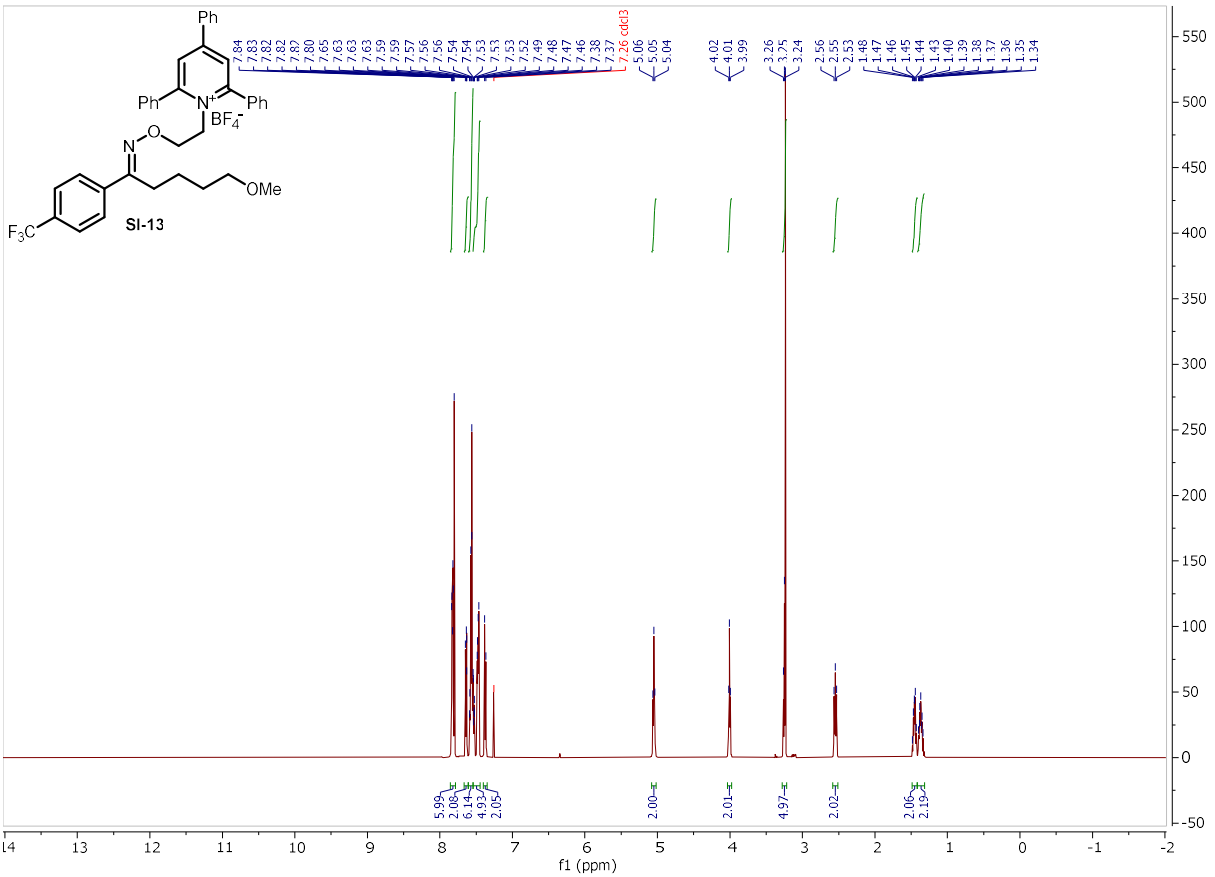
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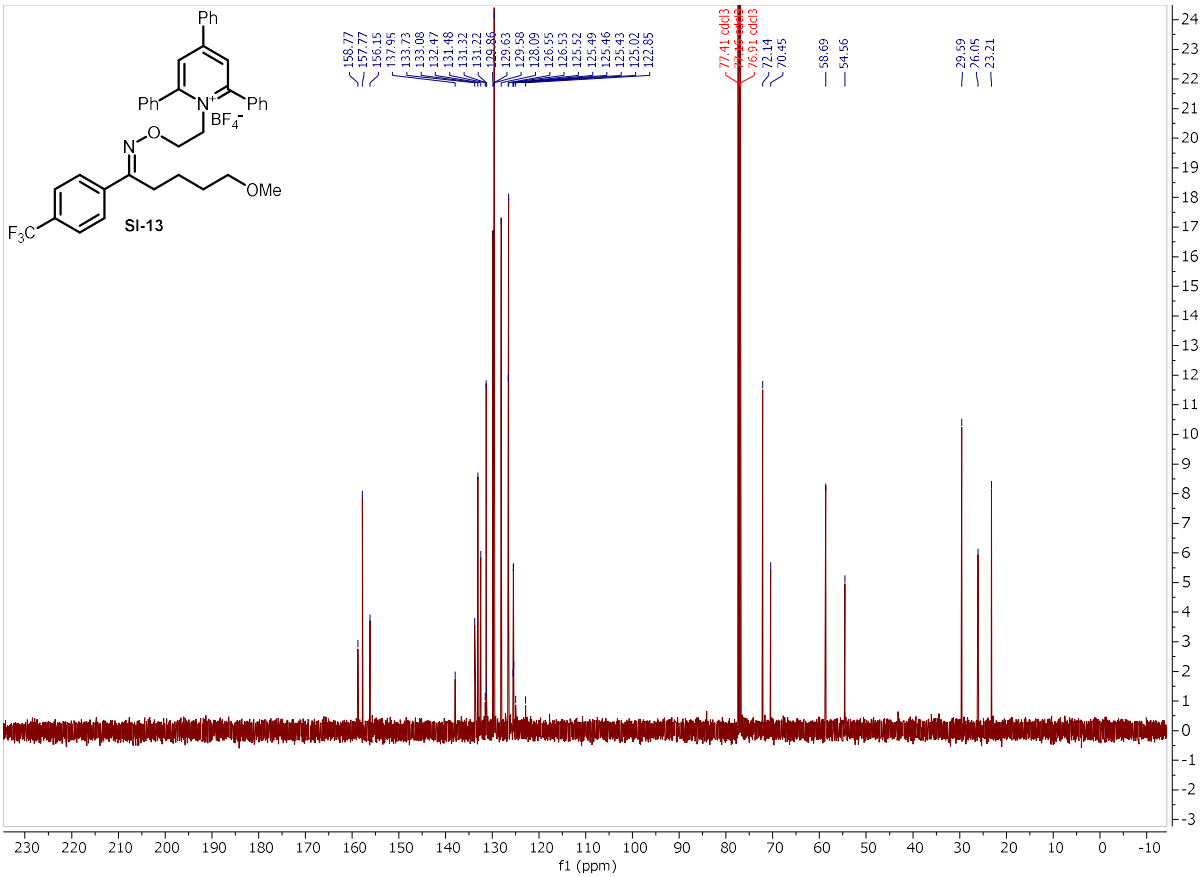
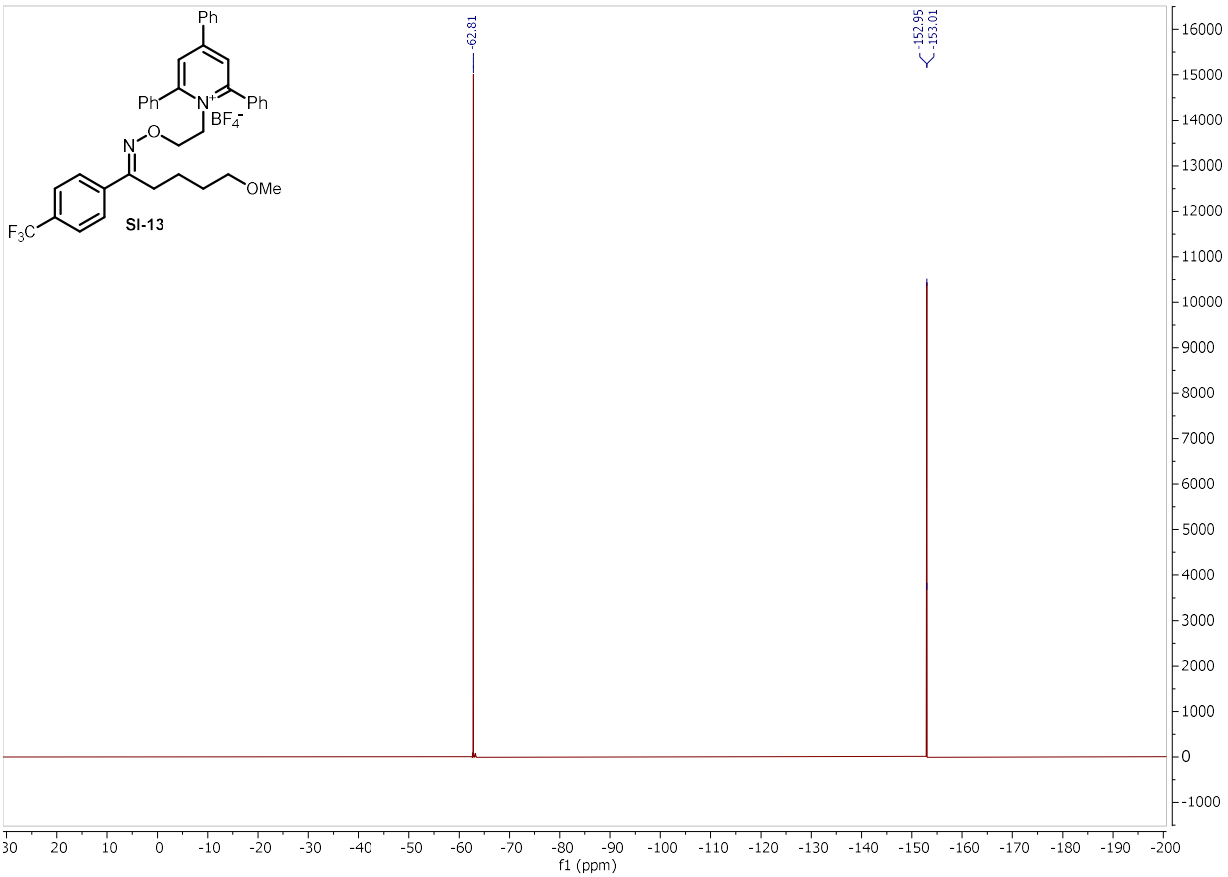
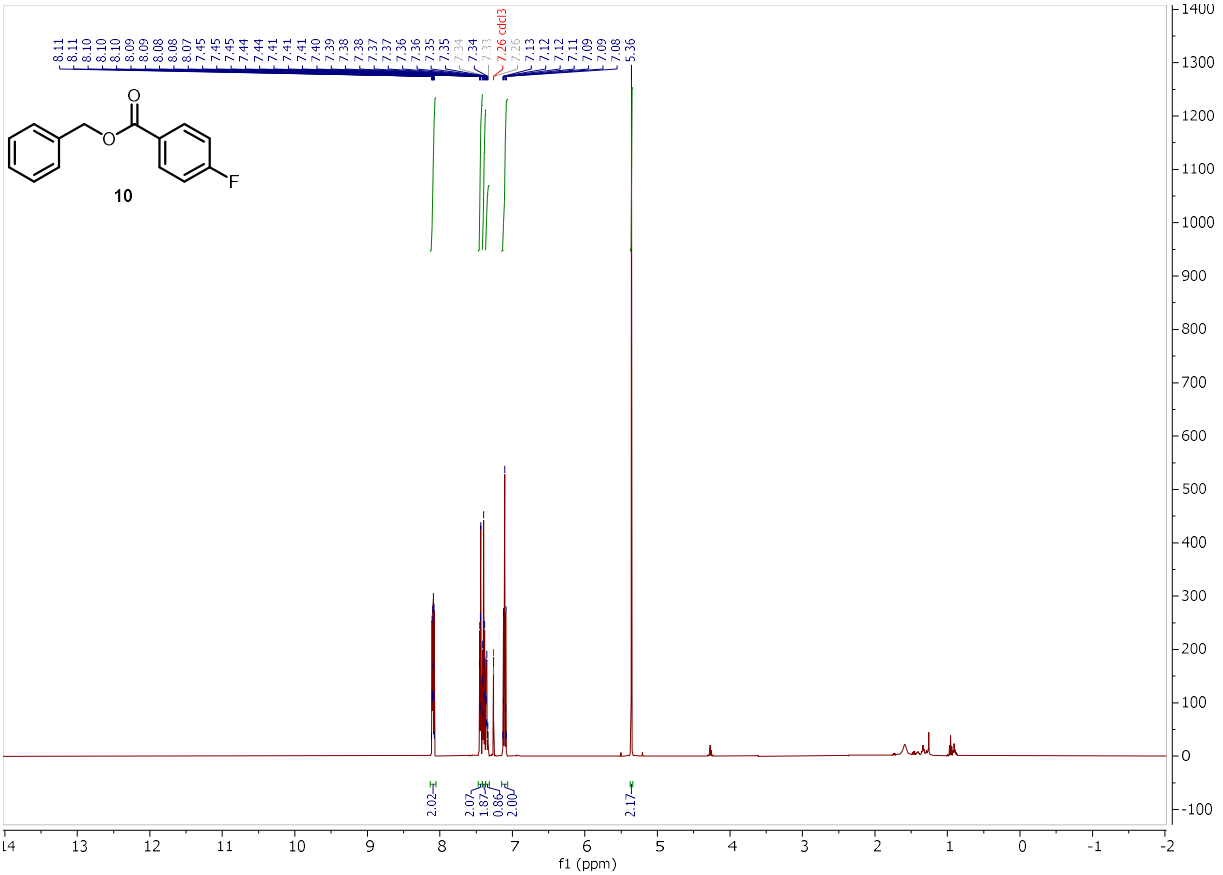
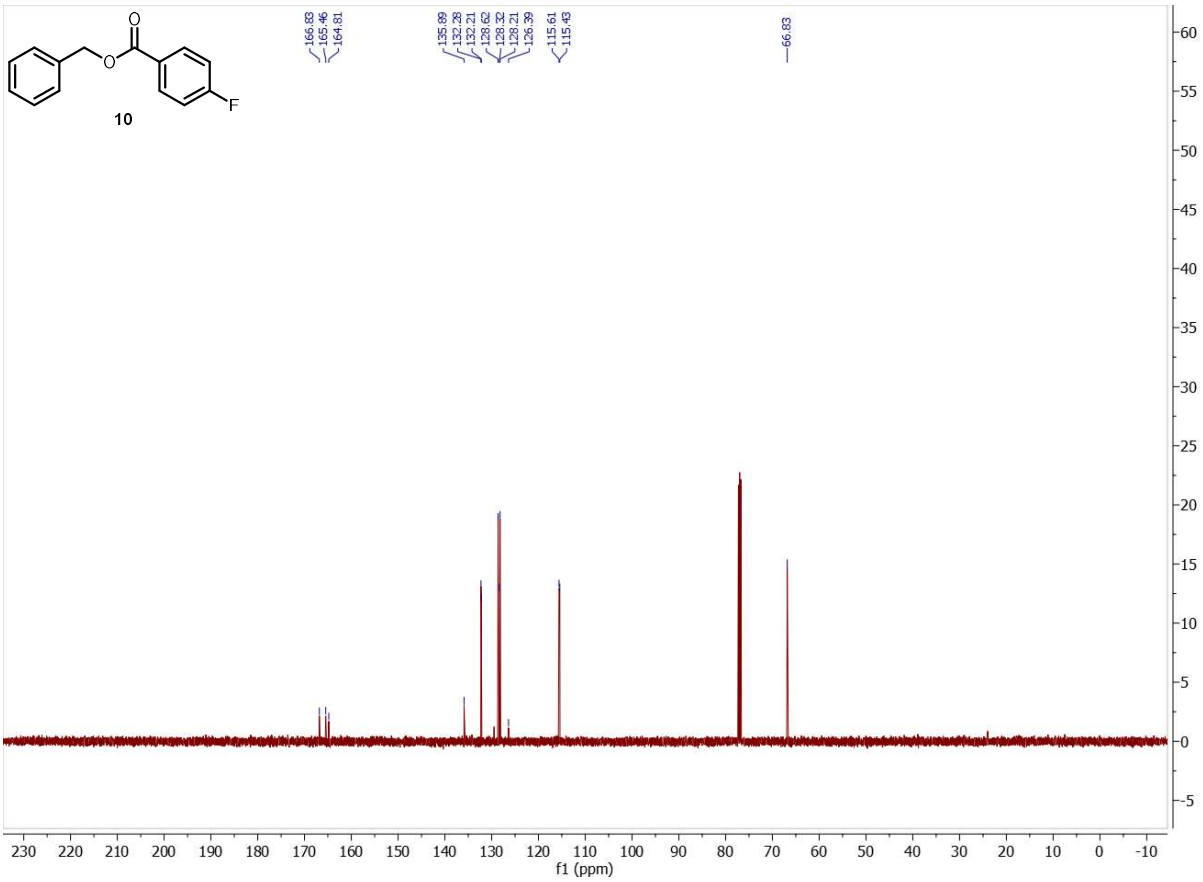
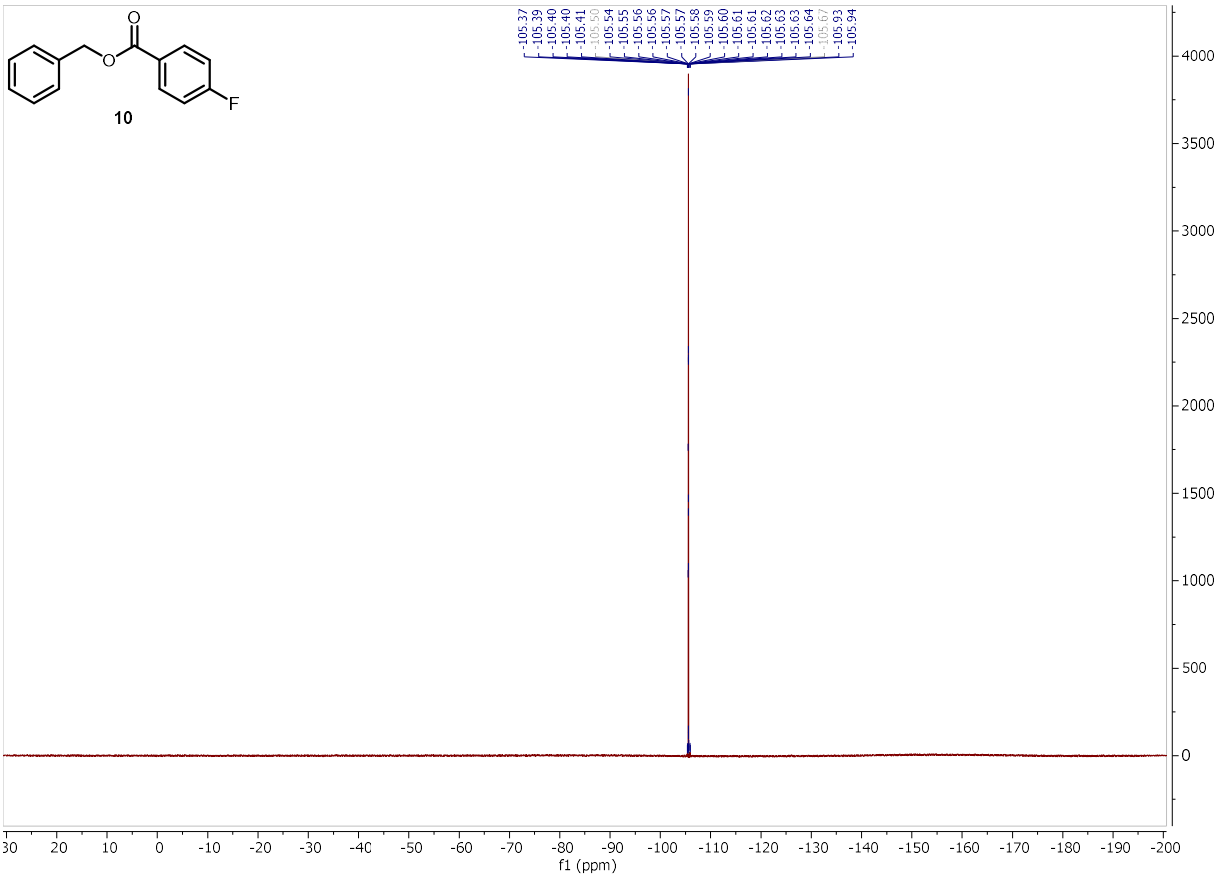
SI-13
f1 (ppm)

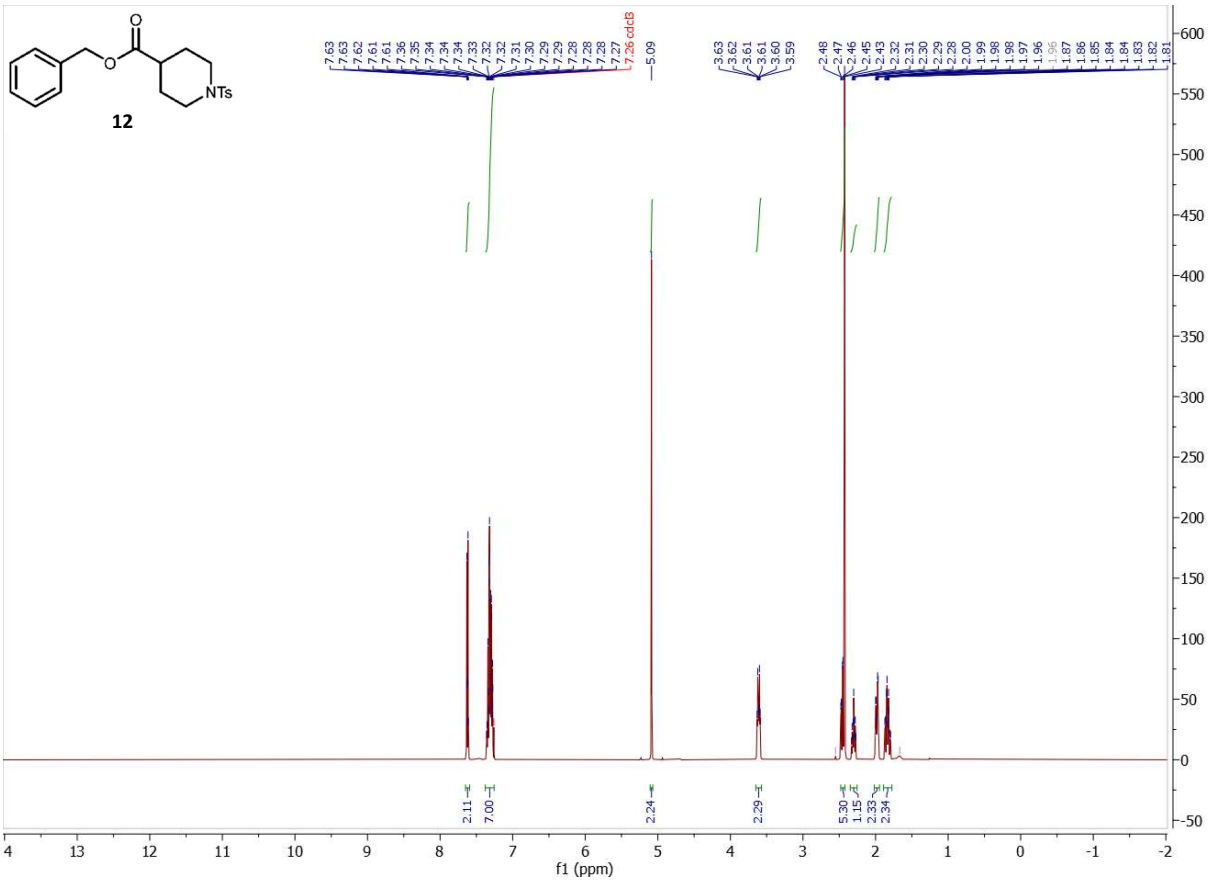

Ph
Ph
N+
Ph
BF4-
N
O
OMe
F3C
SI-13
158.77
157.77
156.15
137.95
133.73
133.08
132.47
131.48
131.32
131.22
129.86
129.63
129.58
128.09
126.55
126.53
125.52
125.49
125.46
125.43
125.02
122.85
77.41 cdcl3
76.91 cdcl3
72.14
70.45
58.69
54.56
29.59
26.05
23.21
f1 (ppm)


Ph
Ph
N+
Ph
BF4-
N
O
OMe
F3C
SI-13
-62.81
-152.95
-153.01
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


10
f1 (ppm)


O
O
F
10
166.83
165.46
164.81
135.69
132.28
132.21
128.62
128.32
128.21
126.39
115.61
115.43
66.83
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
F
10
-105.37
-105.39
-105.40
-105.40
-105.41
-105.54
-105.55
-105.56
-105.56
-105.57
-105.57
-105.58
-105.59
-105.60
-105.61
-105.61
-105.62
-105.63
-105.63
-105.64
-105.67
-105.93
-105.94
4000
3500
3000
2500
2000
1500
1000
500
0
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


12
NTs
7.63
7.63
7.62
7.61
7.61
7.36
7.35
7.34
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.26 cdcl3
5.09
3.63
3.62
3.61
3.61
3.60
3.59
2.48
2.47
2.46
2.45
2.43
2.32
2.31
2.30
2.29
2.28
2.00
1.99
1.98
1.98
1.97
1.96
1.96
1.87
1.86
1.85
1.84
1.84
1.83
1.82
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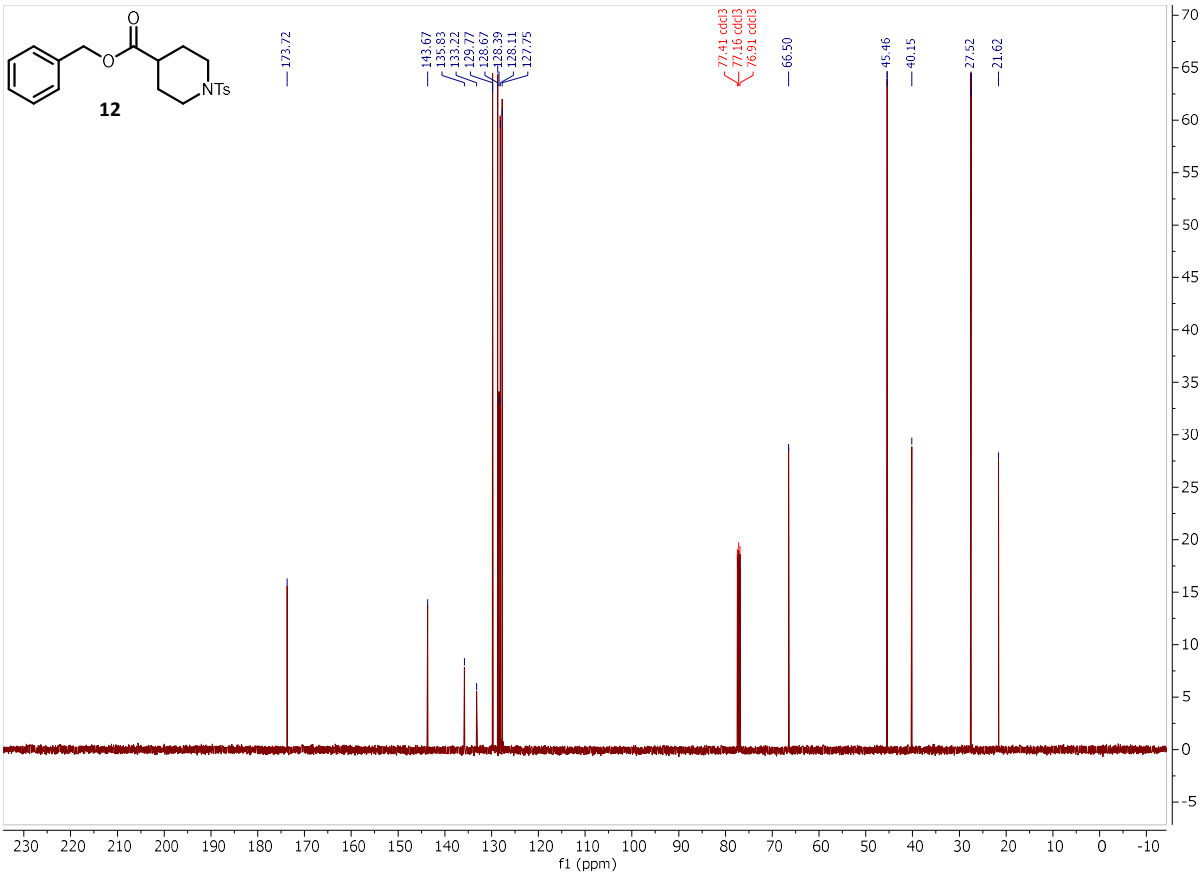
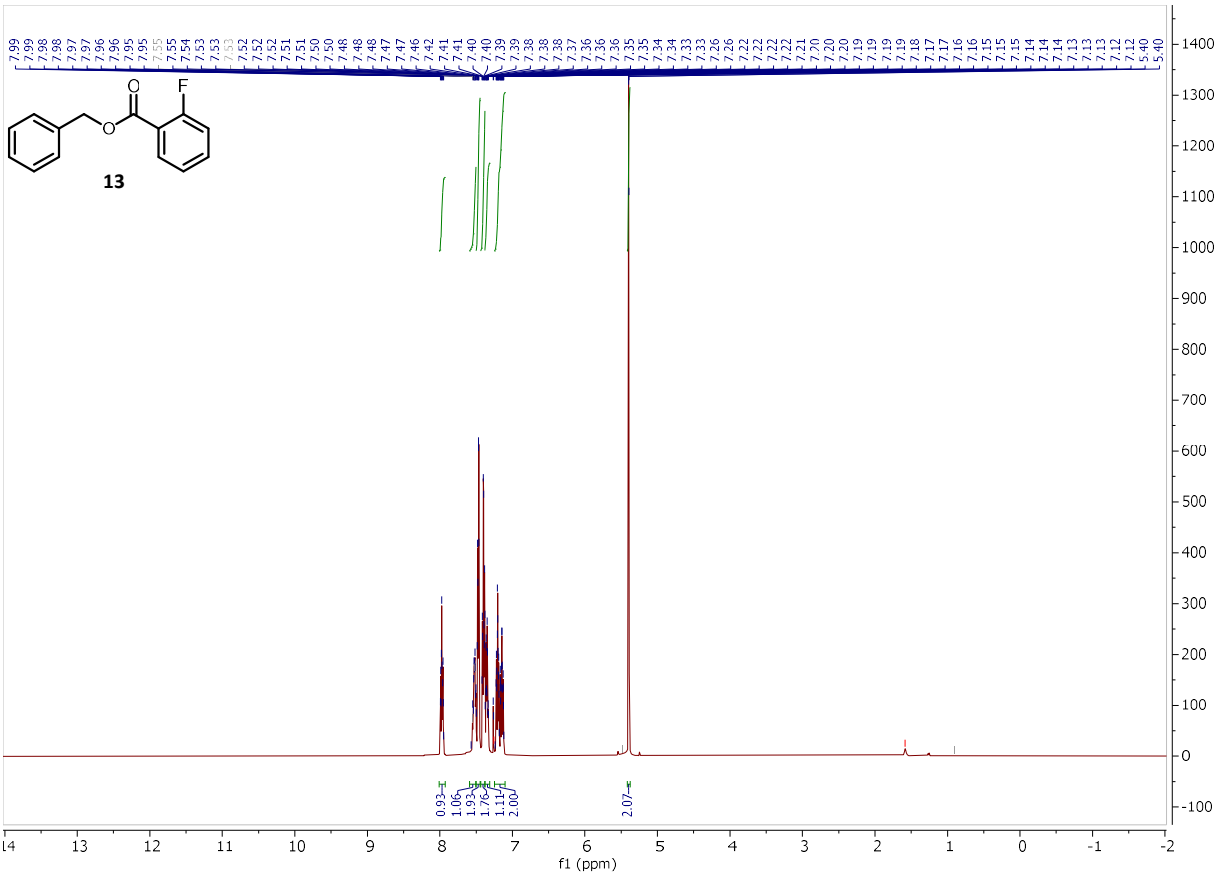
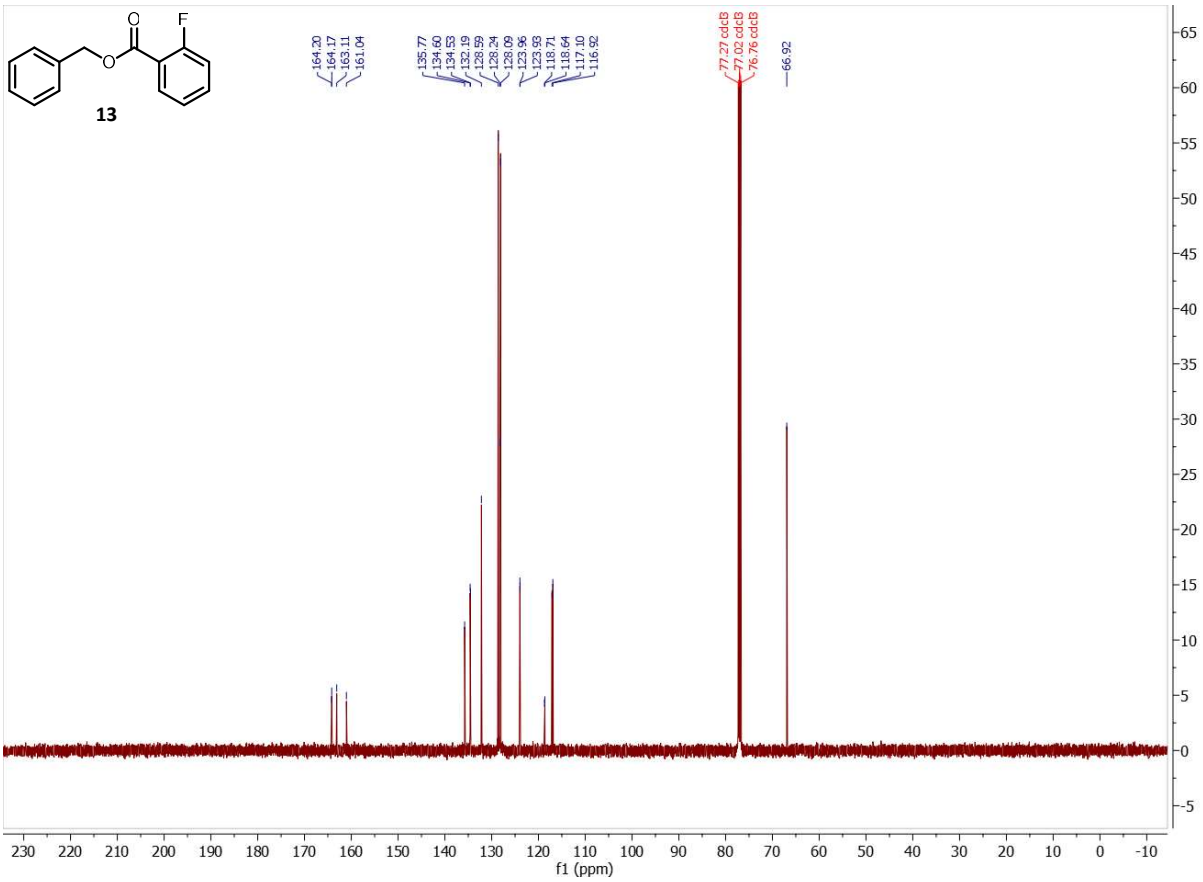
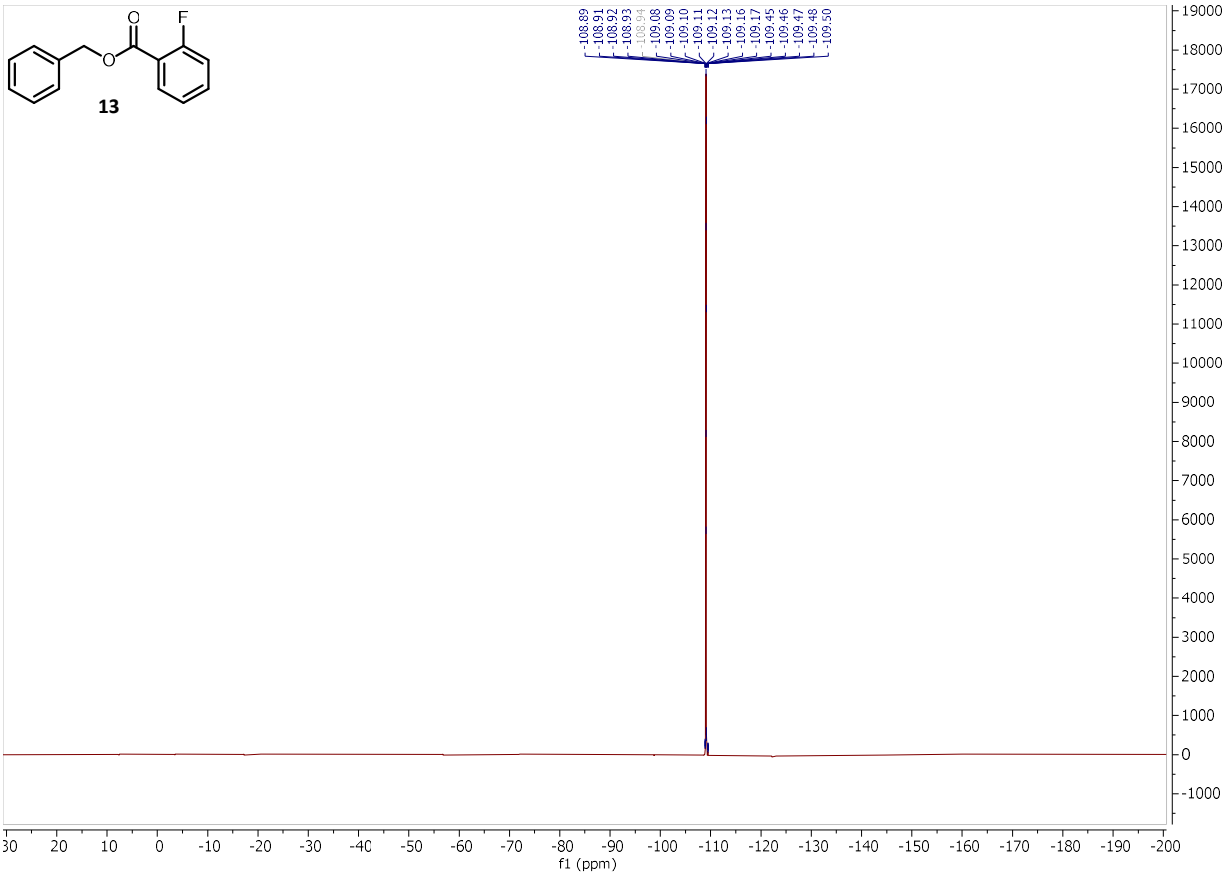
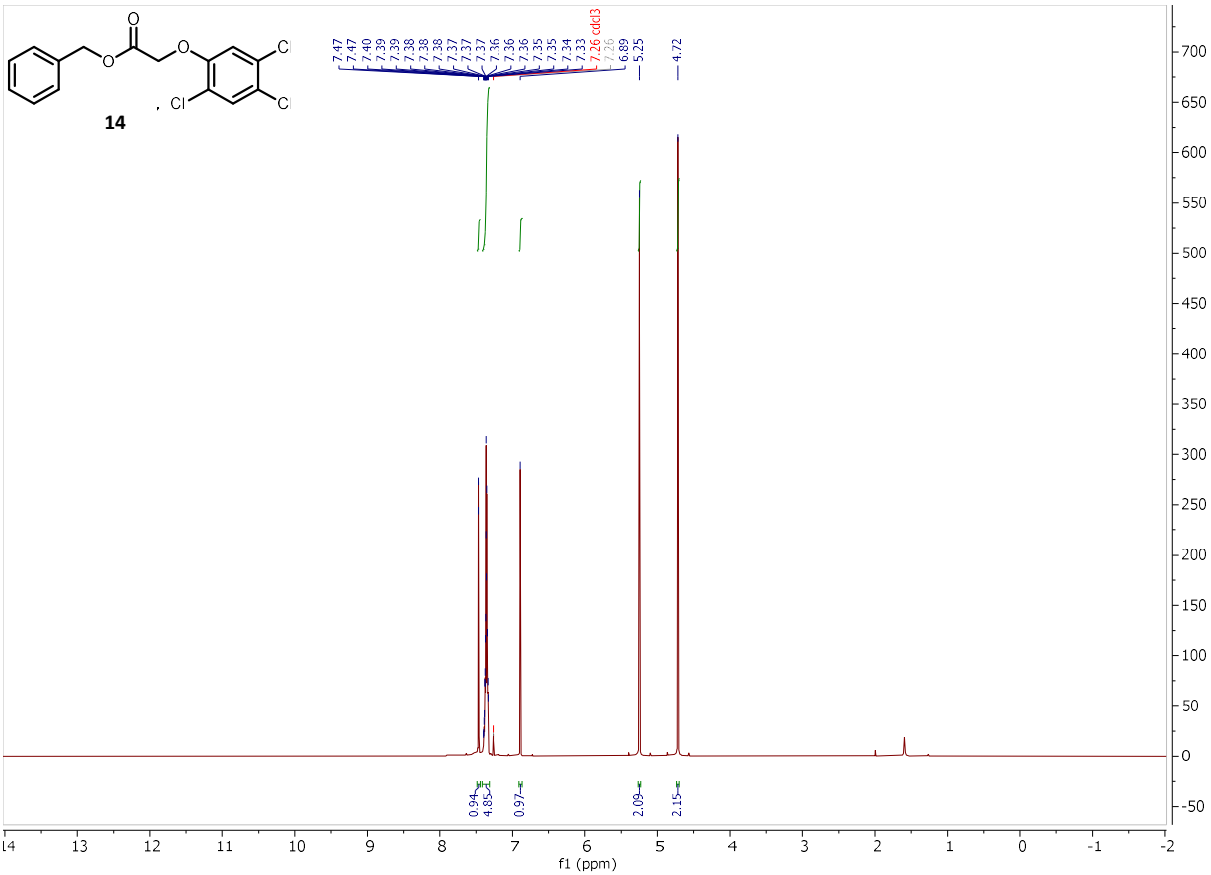
2.11
7.00
2.24
2.29
5.30
1.15
2.33
2.34
f1 (ppm)

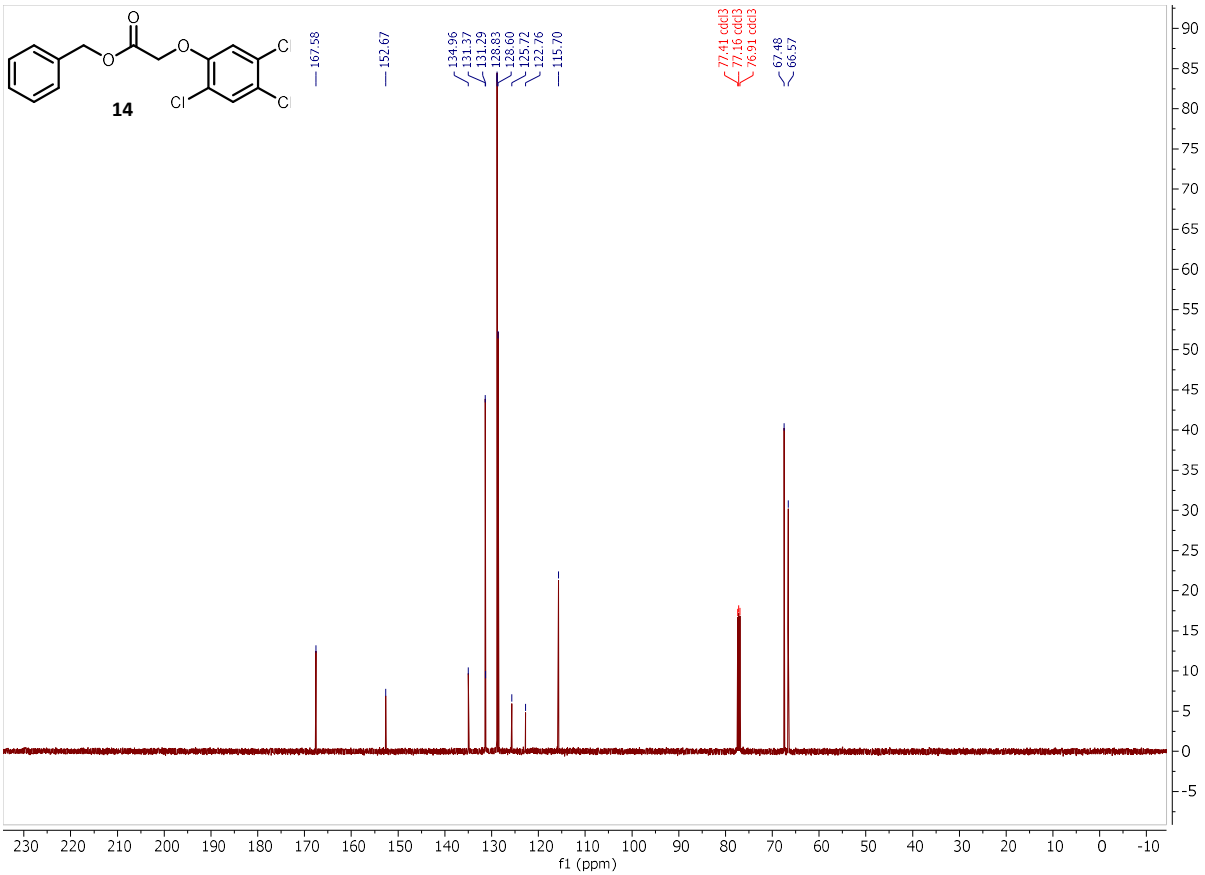

O
O
NTs
12
173.72
143.67
135.83
133.22
129.77
128.67
128.39
128.11
127.75
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
66.50
45.46
40.15
27.52
21.62
f1 (ppm)

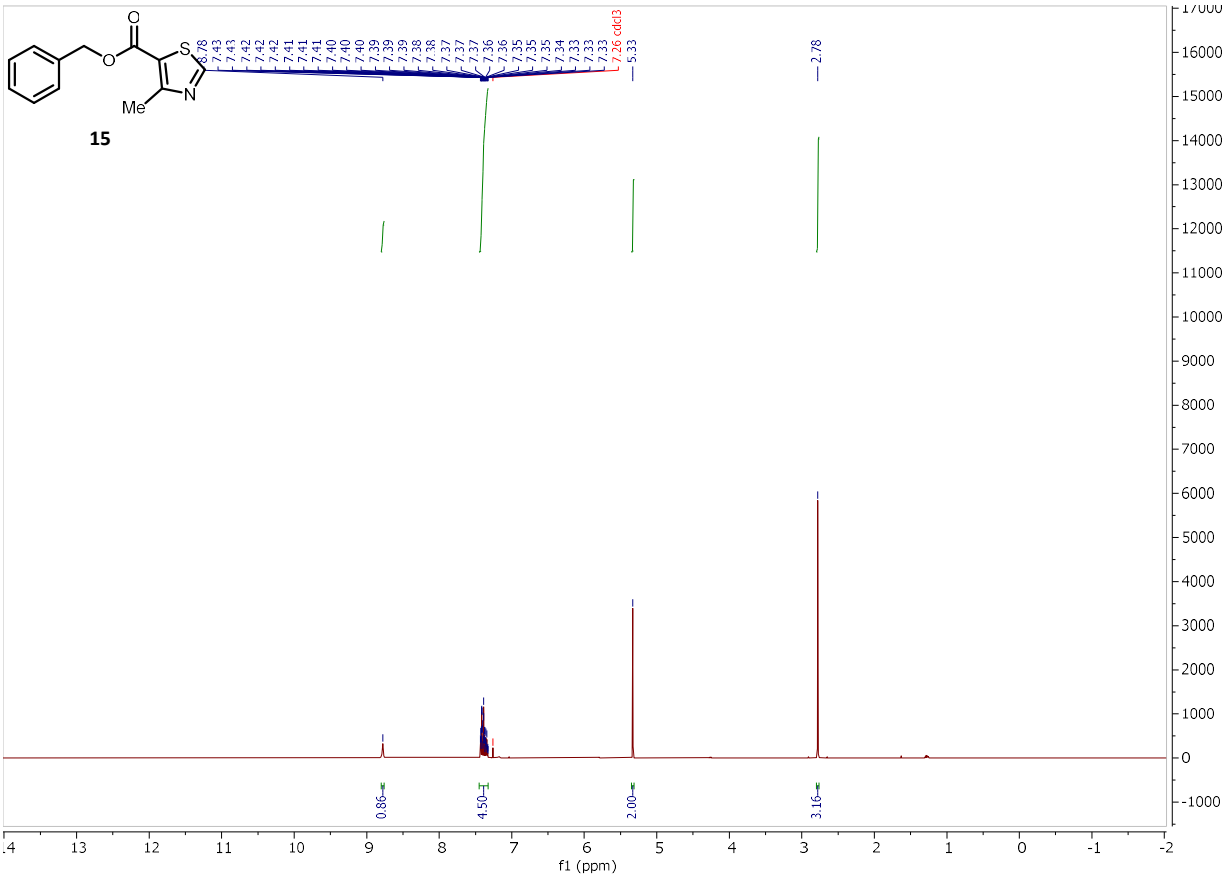

O
F
O
13
f1 (ppm)

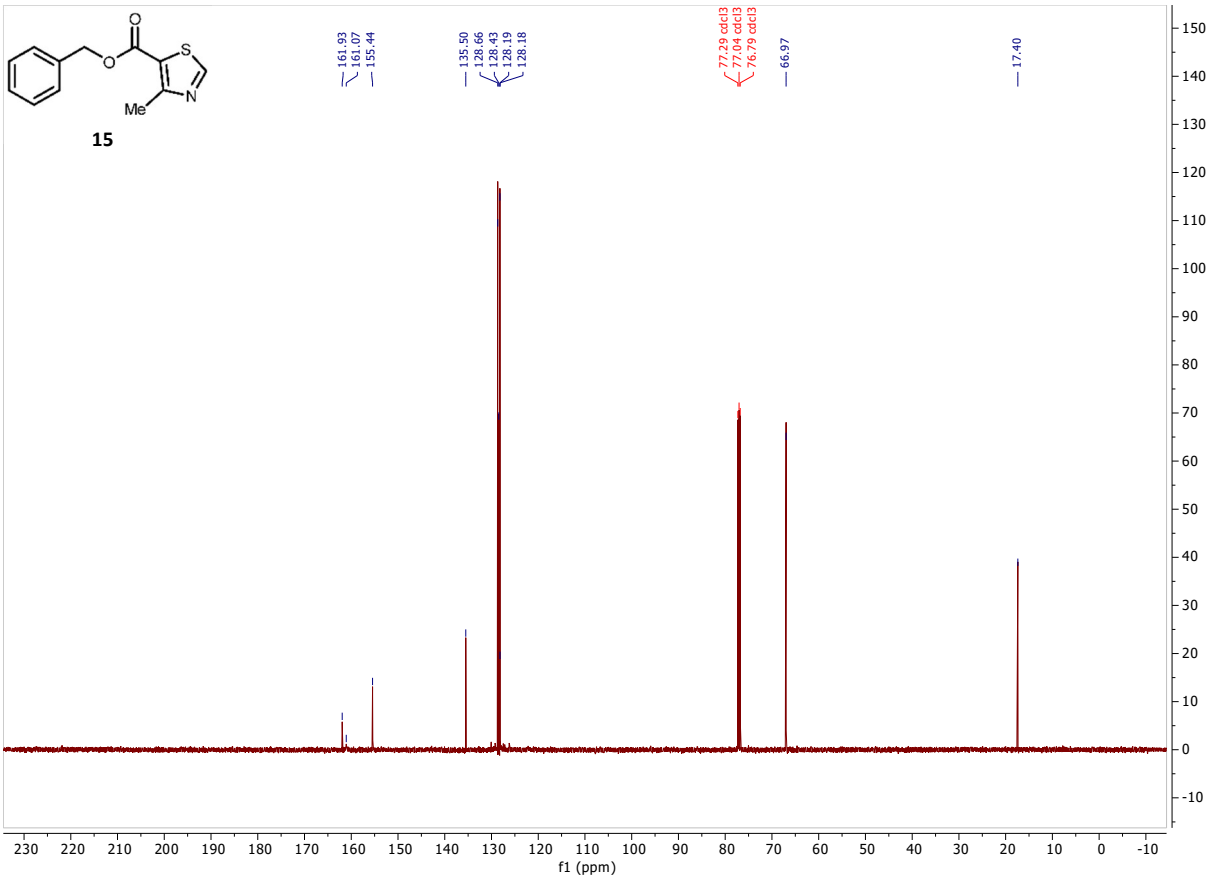

O
F
O
13
164.20
164.17
163.11
161.04
135.77
134.60
134.53
132.19
128.59
128.24
128.09
123.96
123.93
118.71
118.64
117.10
116.92
77.27 cdcl3
77.02 cdcl3
76.76 cdcl3
66.92
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

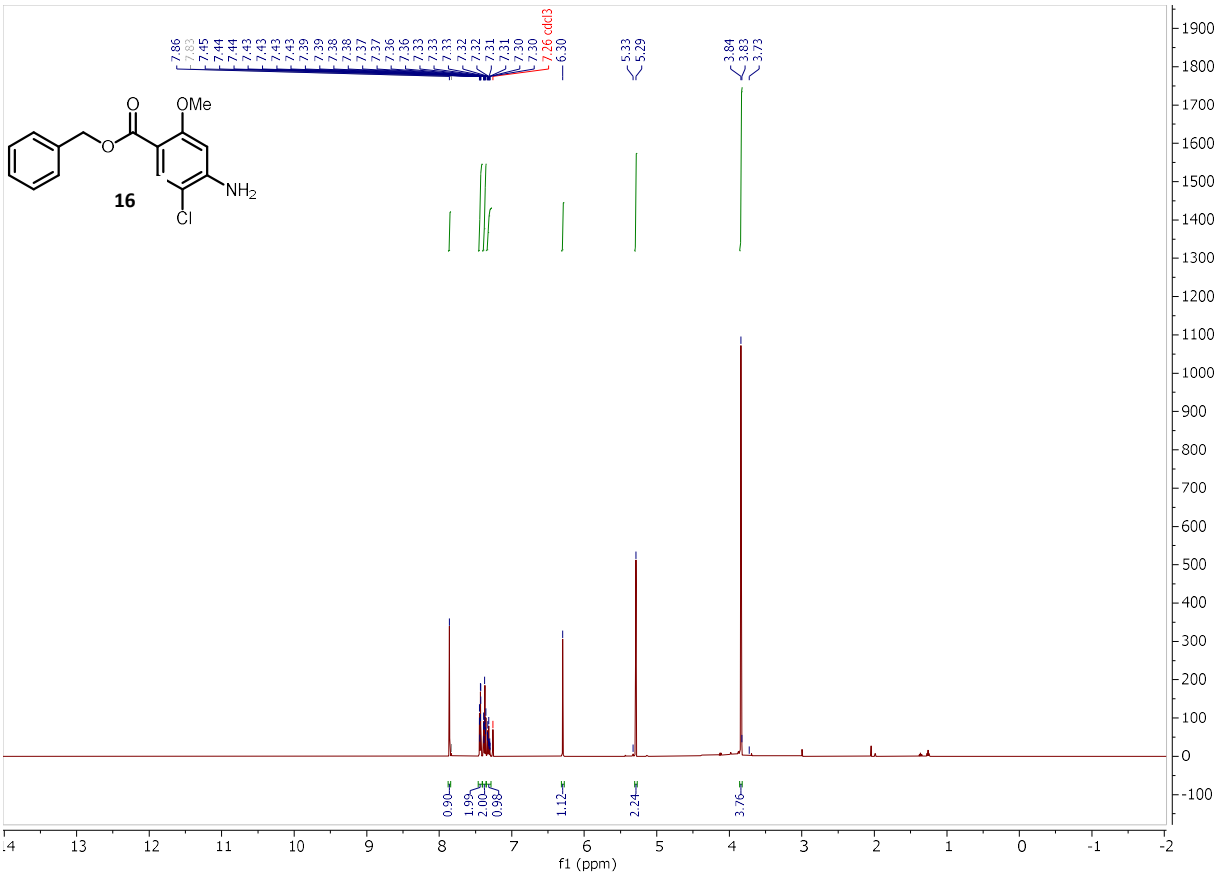

O
F
O
13
-108.89
-108.91
-108.92
-108.93
-109.08
-109.09
-109.10
-109.11
-109.12
-109.13
-109.16
-109.17
-109.45
-109.46
-109.47
-109.48
-109.50
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

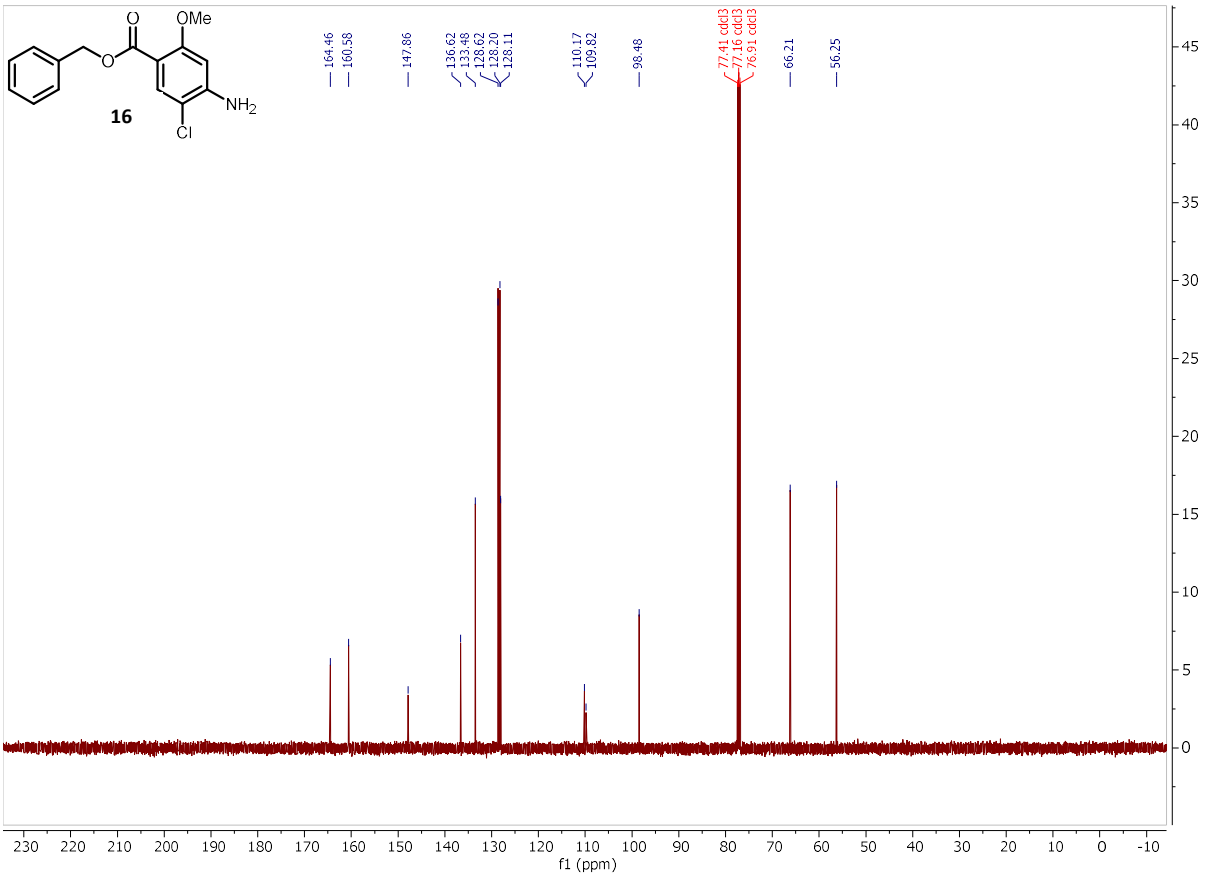

14
7.47
7.47
7.40
7.39
7.39
7.38
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.33
7.26 cdcl3
6.89
5.25
4.72
0.94
4.85
0.97
2.09
2.15
f1 (ppm)

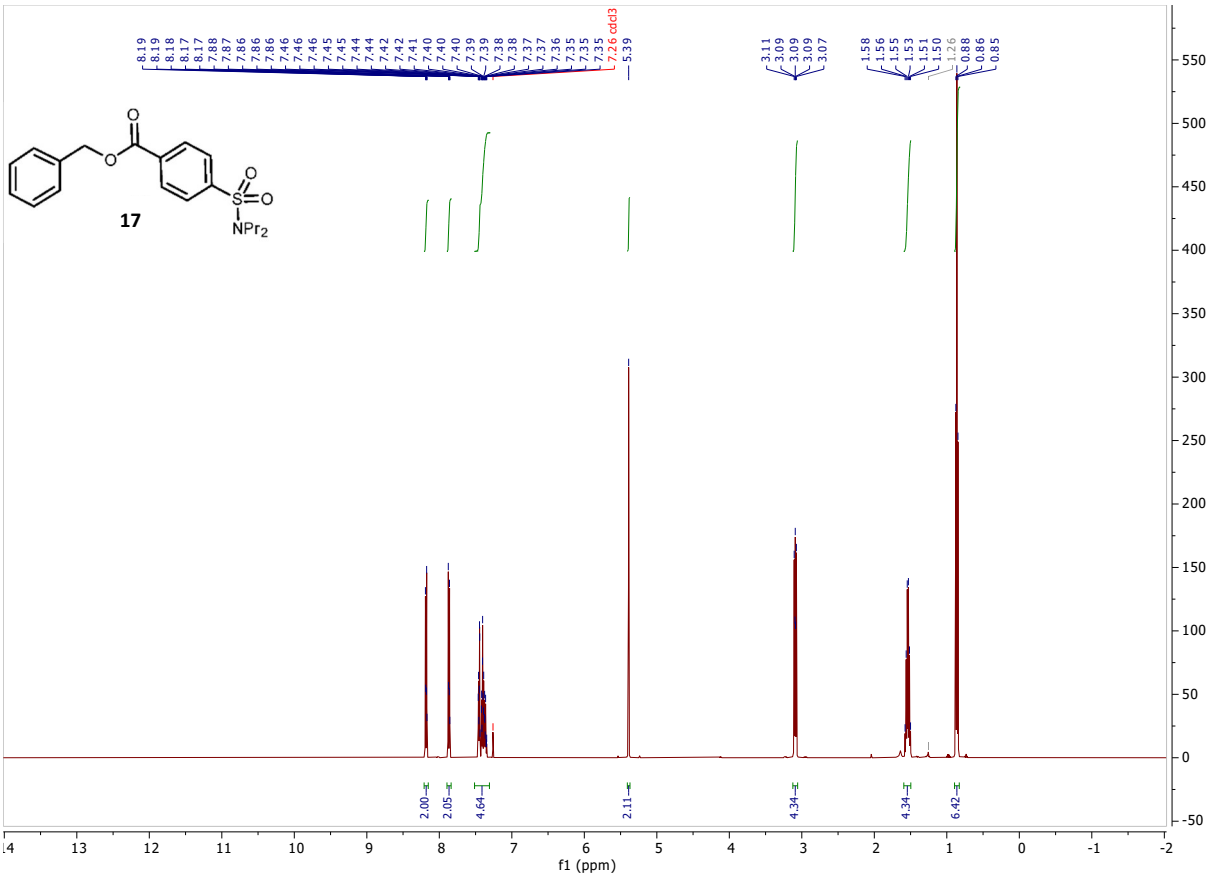

14
167.58
152.67
134.96
131.37
131.29
128.83
128.60
125.72
122.76
115.70
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
67.48
66.57
f1 (ppm)

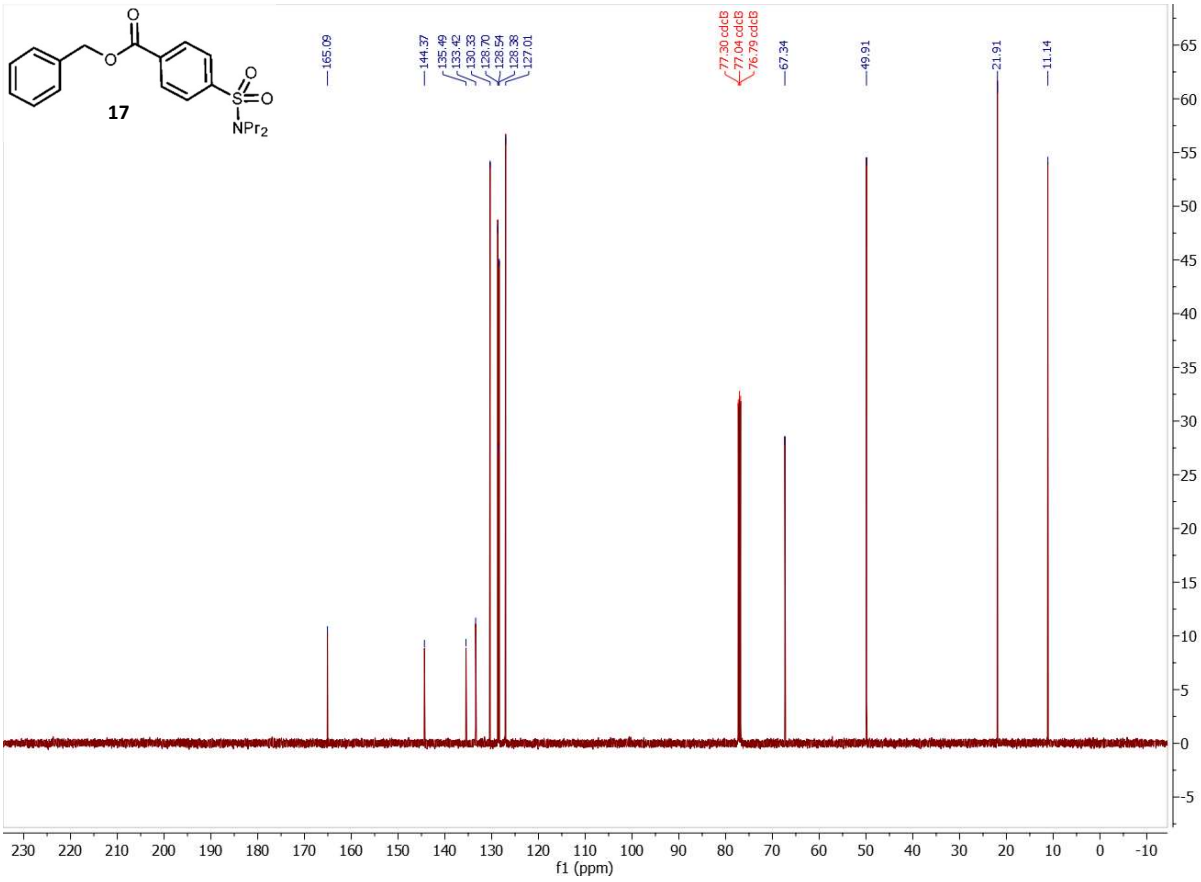

15
Me
7.26 cdcl3
5.33
2.78
0.86
4.50
2.00
3.16
f1 (ppm)

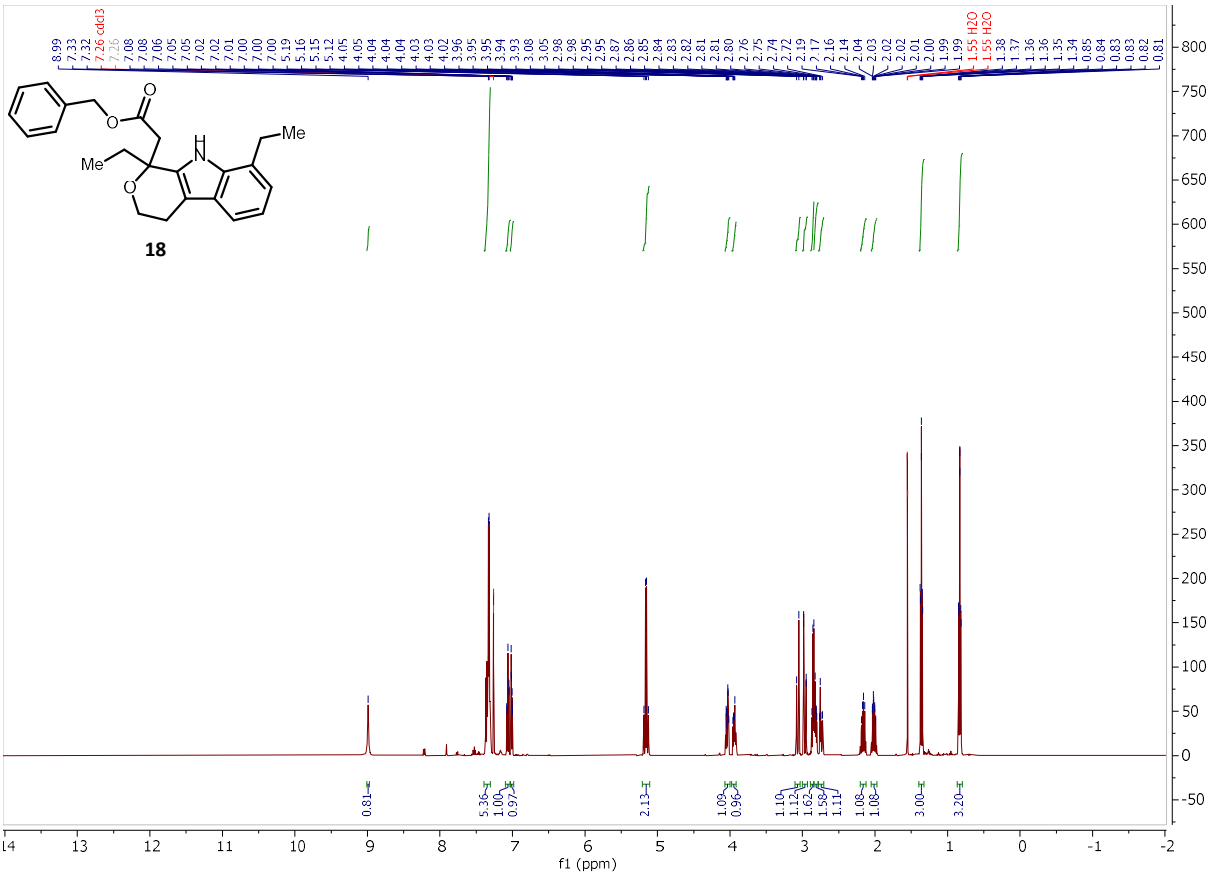

15
161.93
161.07
155.44
135.50
128.66
128.43
128.19
128.18
77.29 cdcl3
77.04 cdcl3
76.79 cdcl3
66.97
17.40
f1 (ppm)

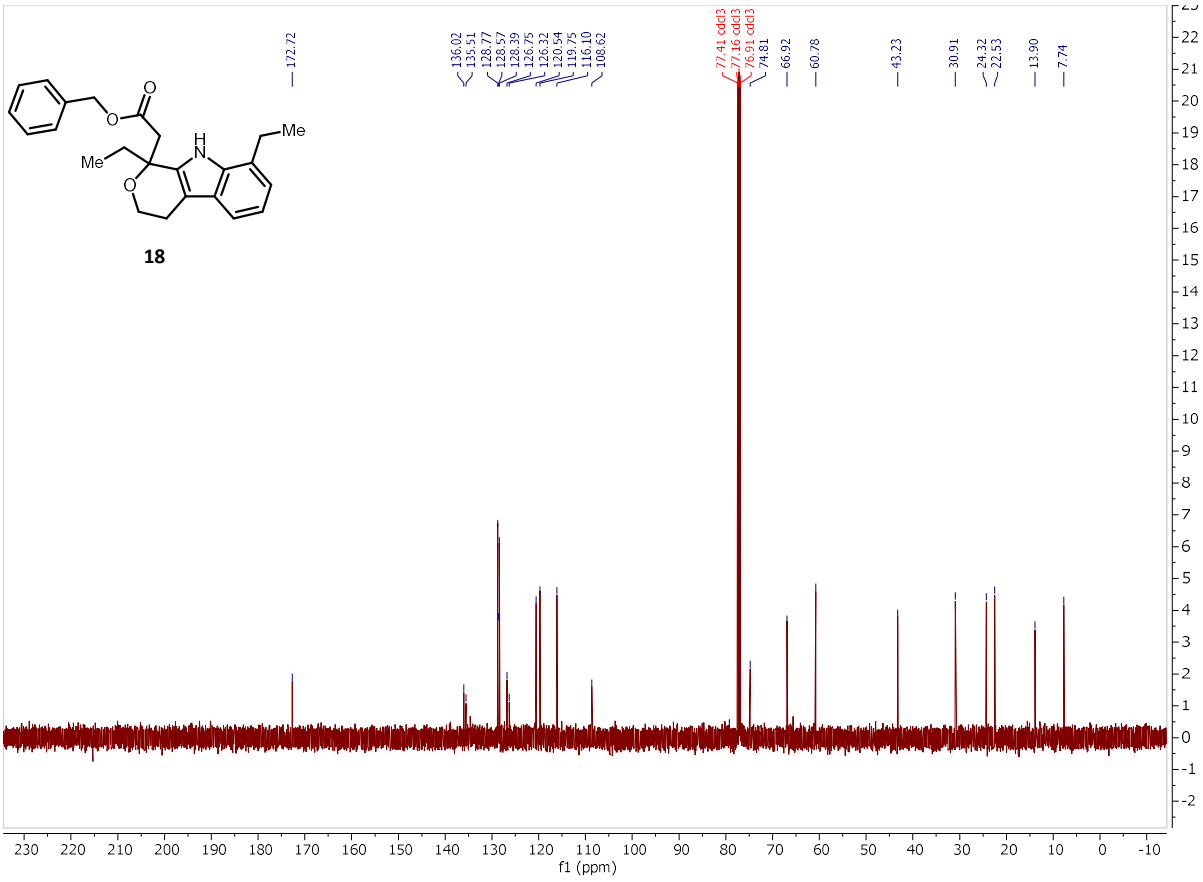

16
OMe
NH2
Cl
f1 (ppm)

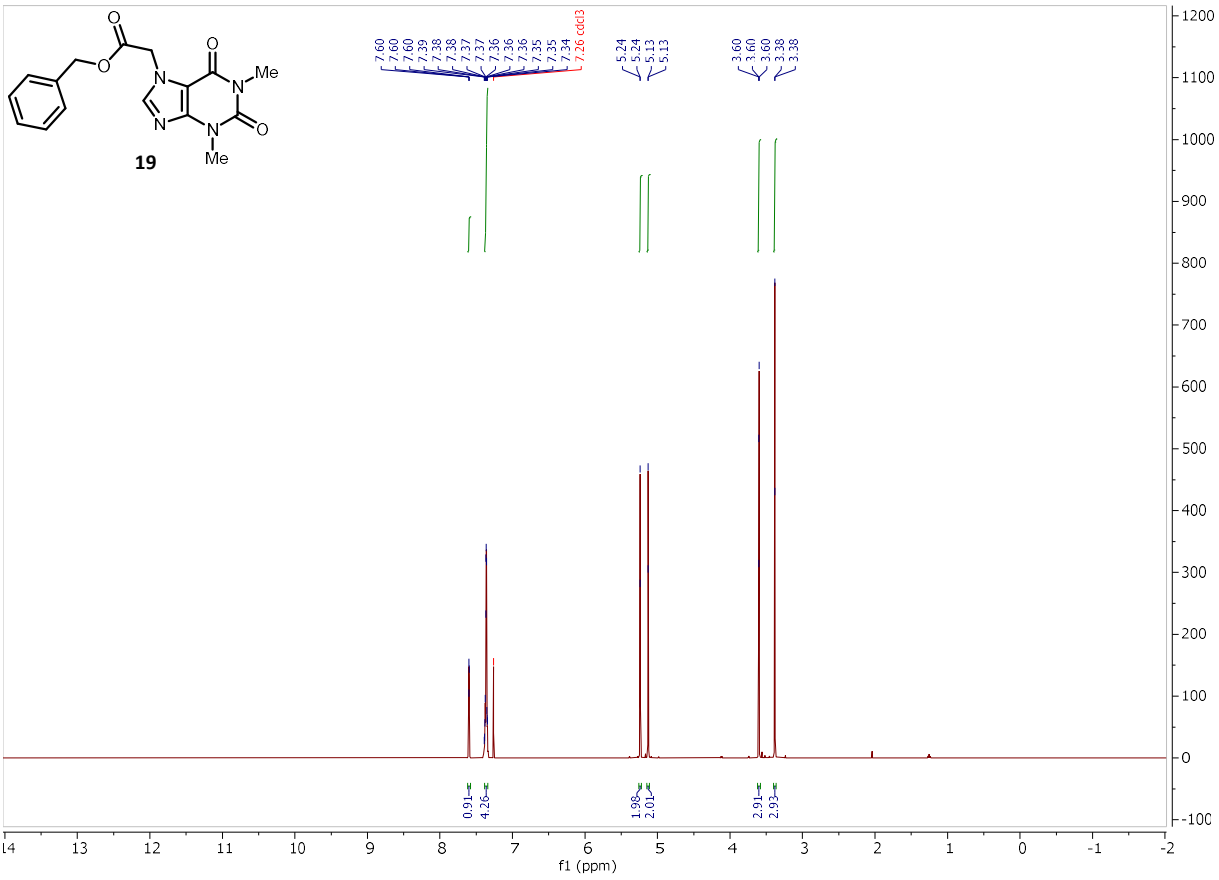

16
O
OMe
O
NH2
Cl
164.46
160.58
147.86
136.62
133.48
128.62
128.20
128.11
110.17
109.82
98.48
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
66.21
56.25
f1 (ppm)

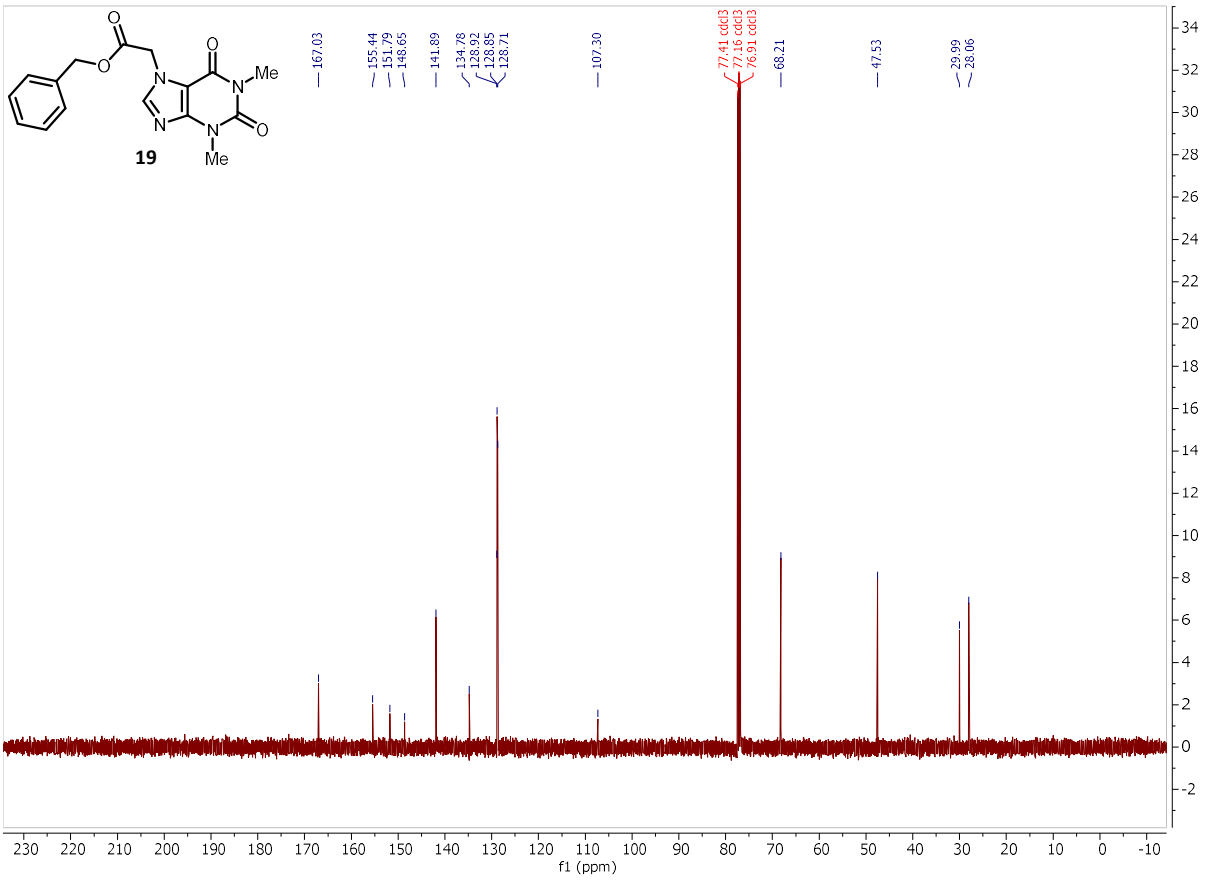

17
NPr2
f1 (ppm)

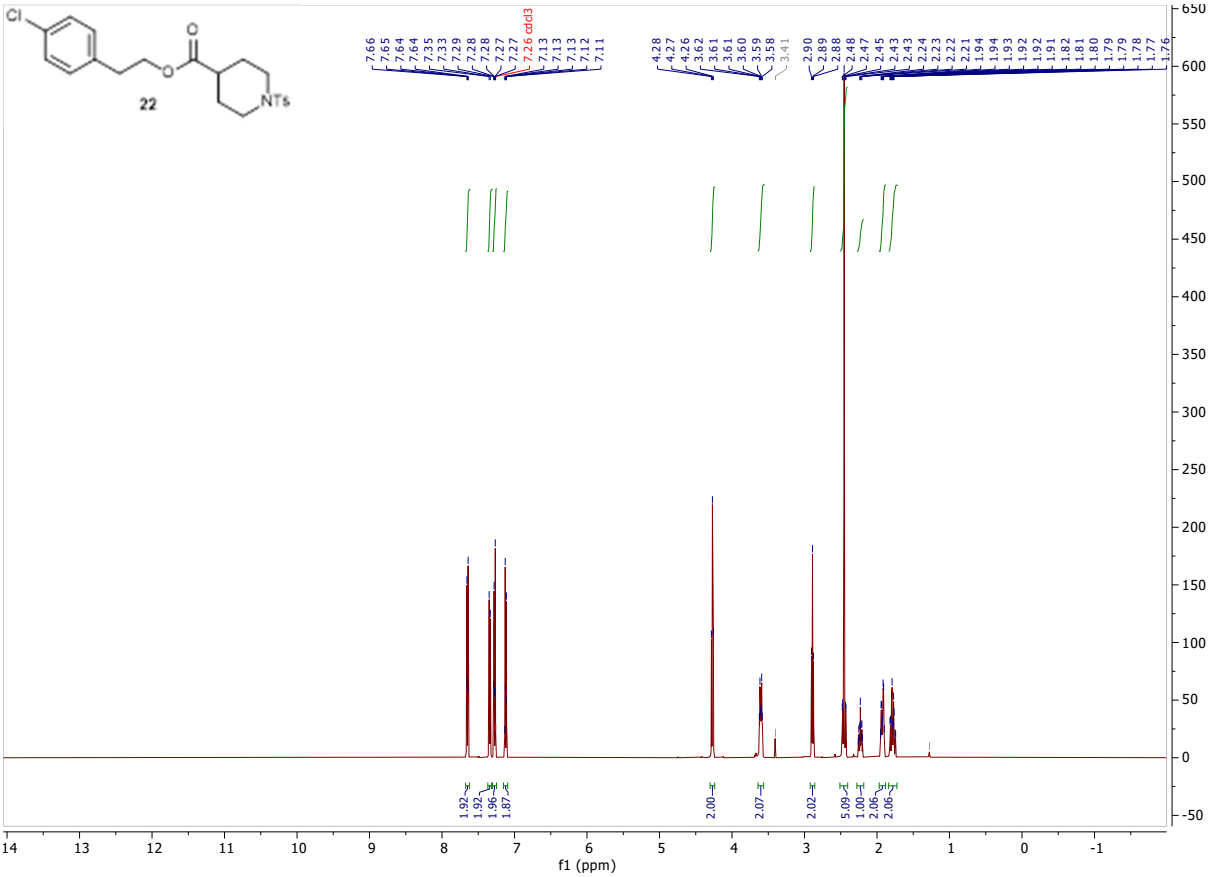

17
165.09
144.37
135.49
133.42
130.33
128.70
128.54
128.38
127.01
77.30 cdcl3
77.04 cdcl3
76.79 cdcl3
67.34
49.91
21.91
11.14
f1 (ppm)

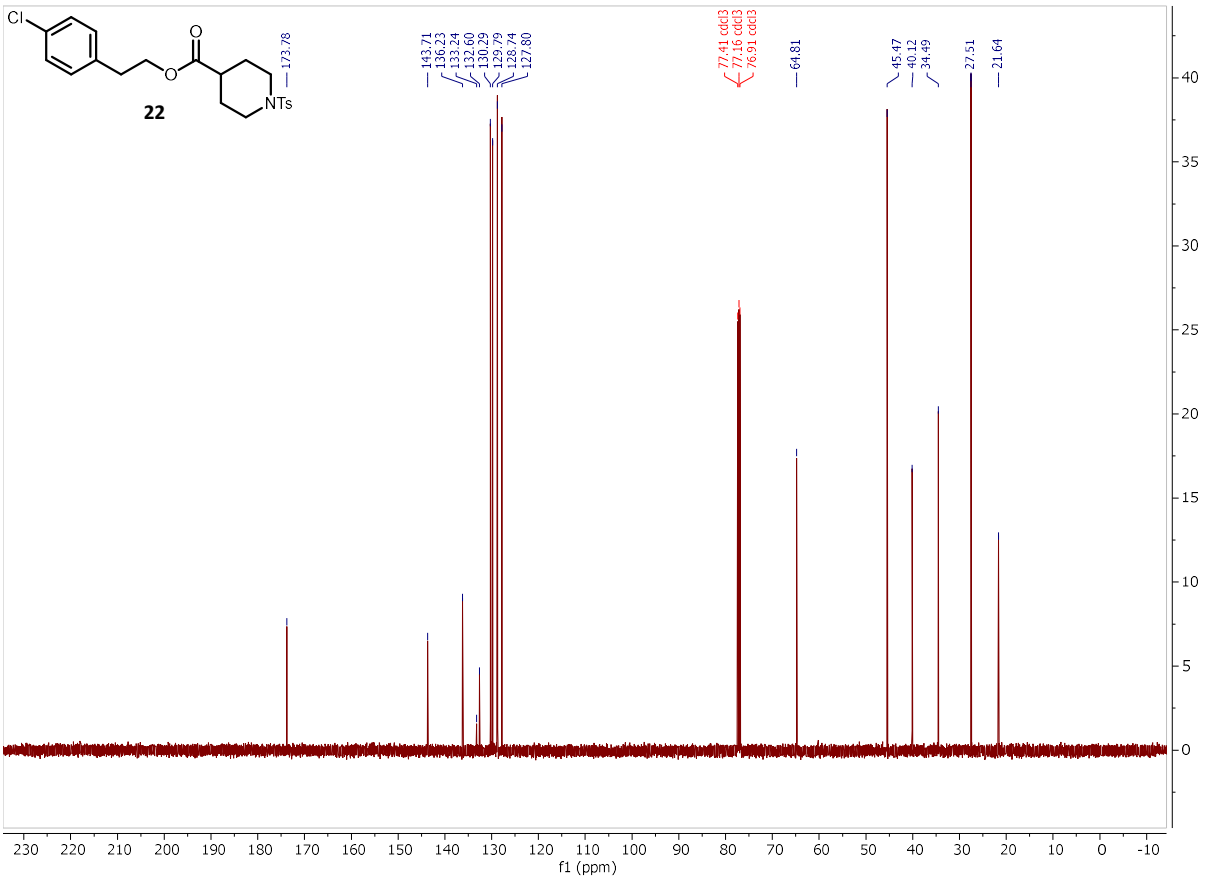

18
f1 (ppm)

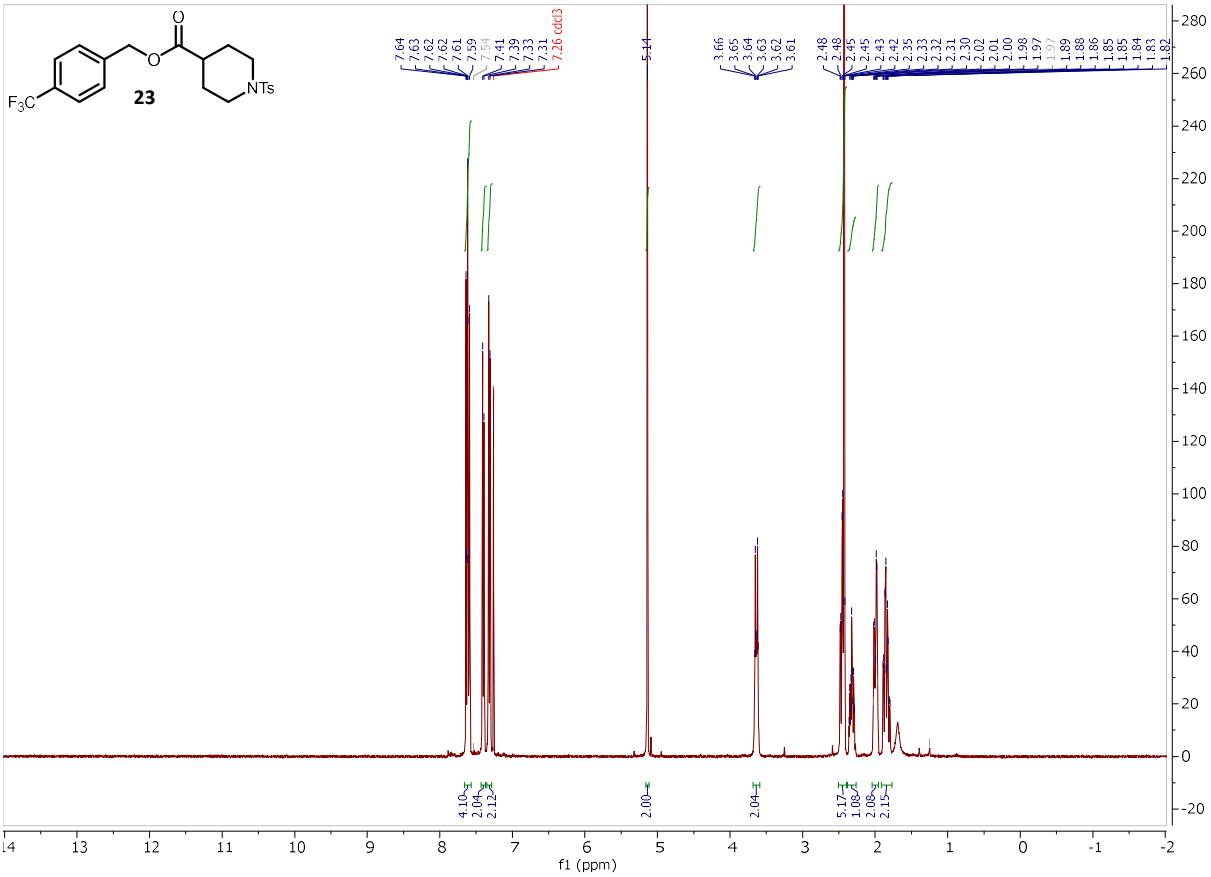

172.72
136.02
135.51
128.77
128.57
128.39
126.75
126.32
120.54
119.75
116.10
108.62
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
74.81
66.92
60.78
43.23
30.91
24.32
22.53
13.90
7.74
O
O
H
N
Me
Me
O
18
f1 (ppm)

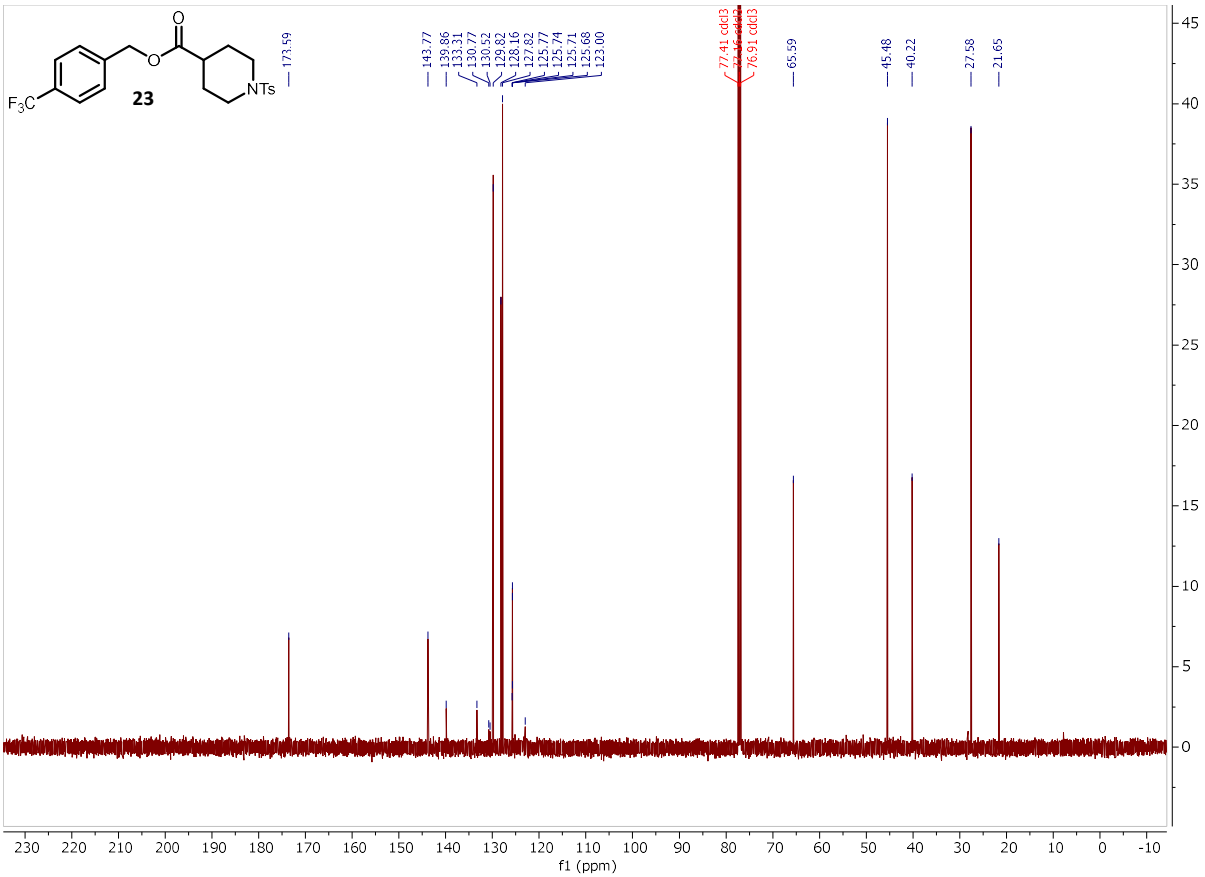

19
7.60
7.60
7.60
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.36
7.35
7.35
7.34
7.26 cdcl3
5.24
5.24
5.13
5.13
3.60
3.60
3.60
3.38
3.38
0.91
4.26
1.98
2.01
2.91
2.93
f1 (ppm)

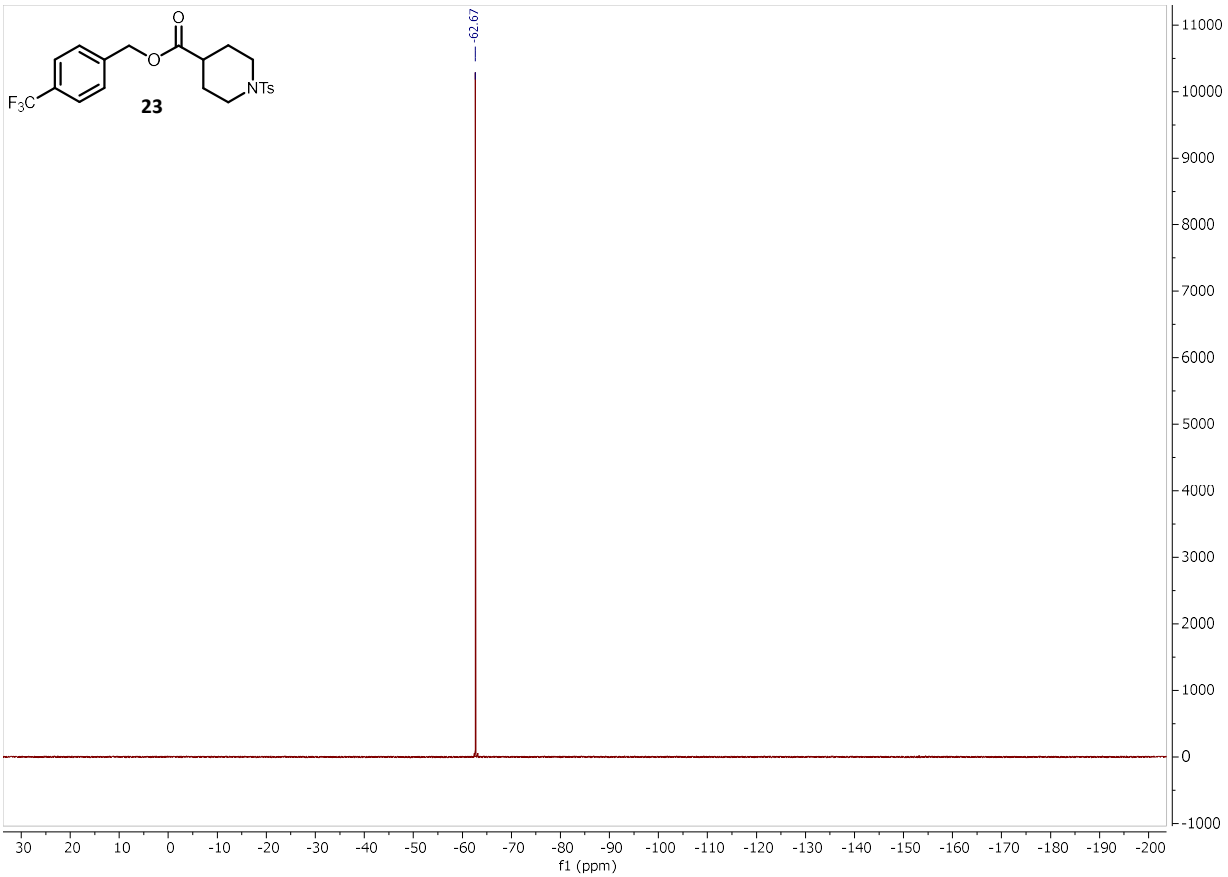

19
167.03
155.44
151.79
148.65
141.89
134.78
128.92
128.85
128.71
107.30
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
68.21
47.53
29.99
28.06
f1 (ppm)

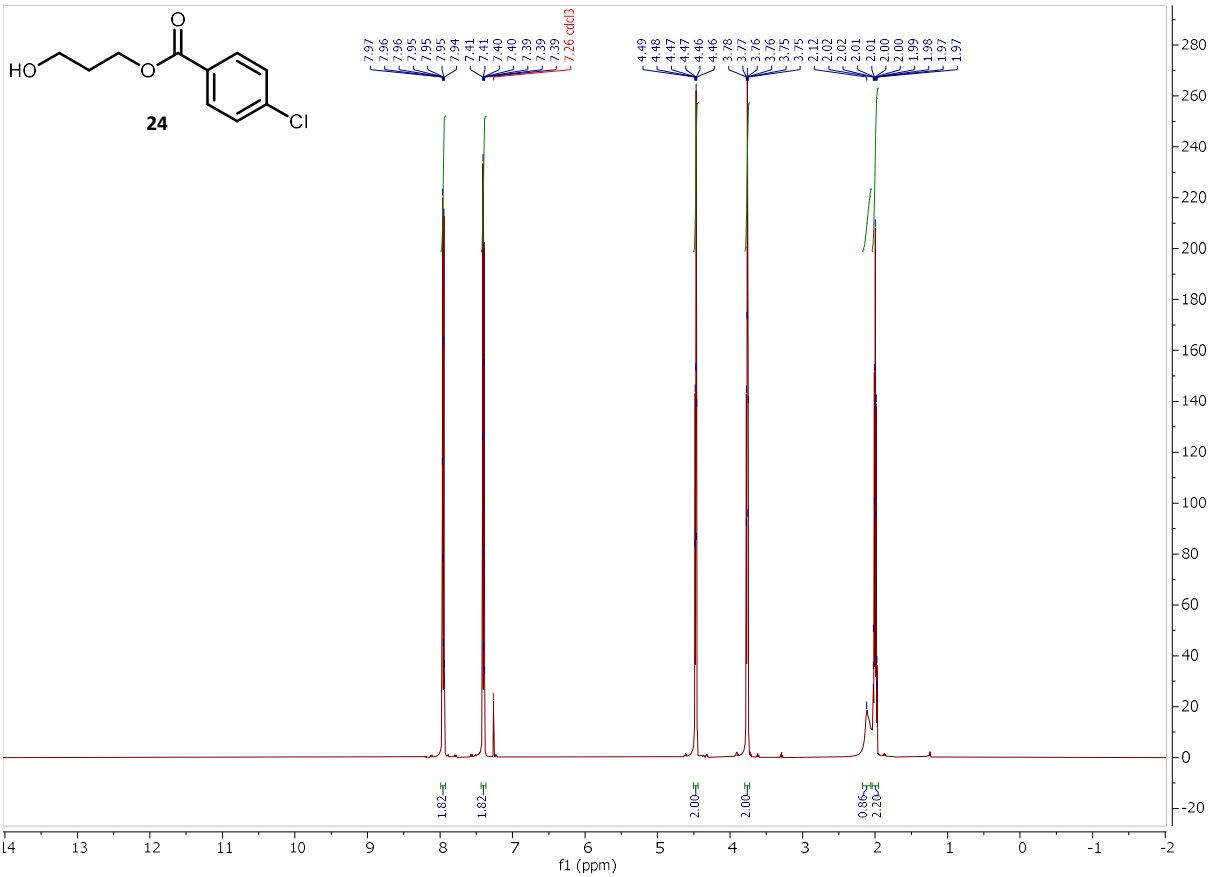

Cl
O
O
NTs
22
7.66
7.65
7.64
7.64
7.35
7.33
7.29
7.28
7.28
7.27
7.27
7.26 cdcl3
7.13
7.13
7.13
7.12
7.11
4.28
4.27
4.26
3.62
3.61
3.61
3.60
3.59
3.58
3.41
2.90
2.89
2.88
2.48
2.47
2.45
2.43
2.43
2.24
2.23
2.22
2.21
1.94
1.94
1.93
1.92
1.92
1.91
1.82
1.81
1.80
1.79
1.79
1.78
1.77
1.76
1.92
1.92
1.96
1.87
2.00
2.07
2.02
5.09
1.00
2.06
2.06
f1 (ppm)

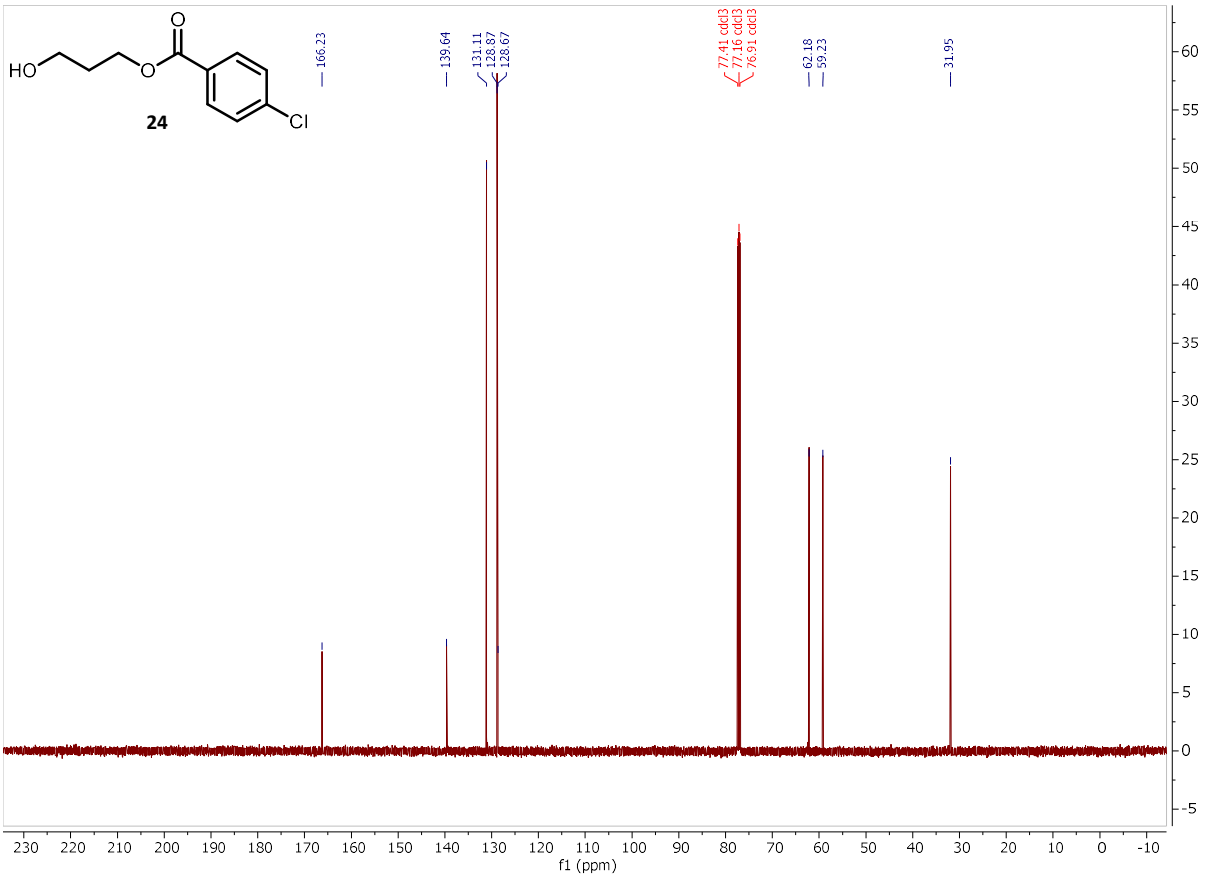

Cl
O
O
NTs
22
173.78
143.71
136.23
133.24
132.60
130.29
129.79
128.74
127.80
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
64.81
45.47
40.12
34.49
27.51
21.64
f1 (ppm)

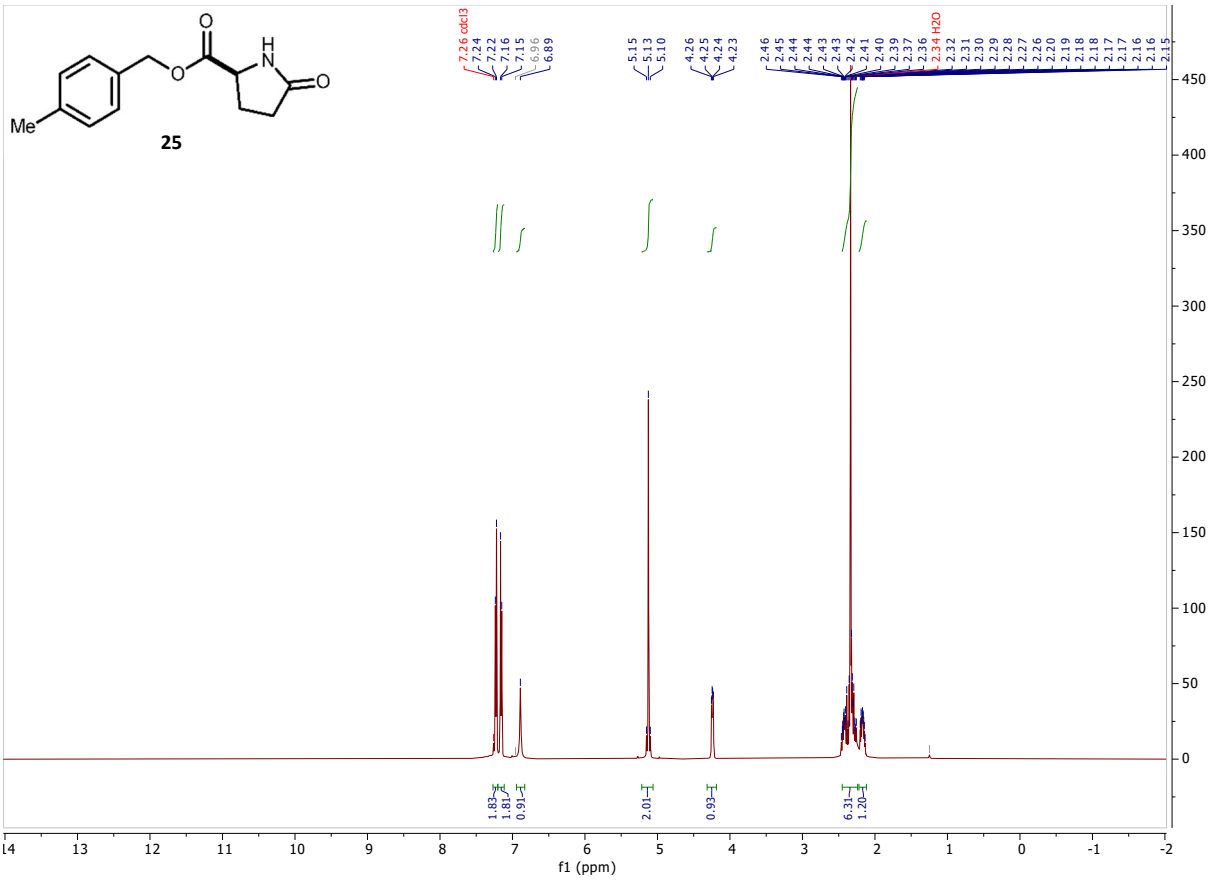

23
F3C
NTs
f1 (ppm)

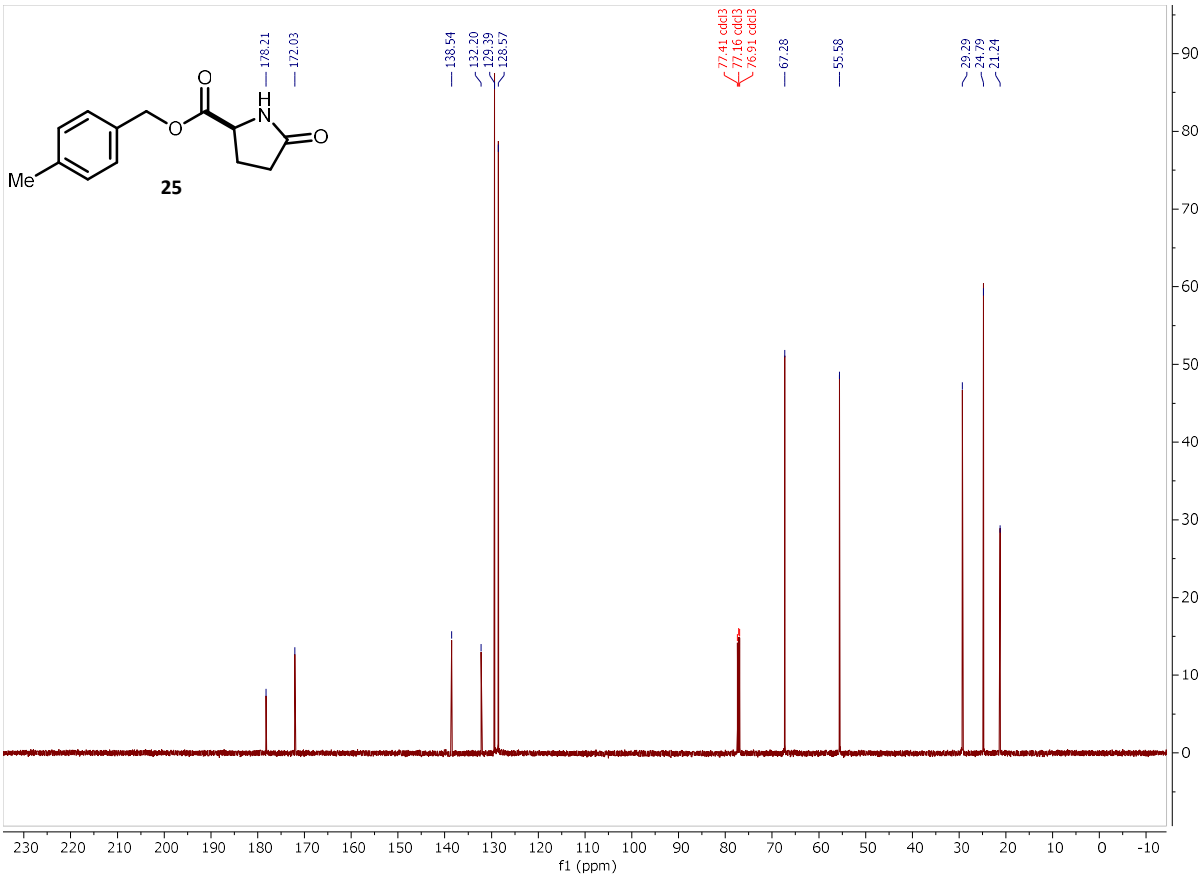

O
O
F3C
NTs
23
171.59
143.77
139.86
133.31
130.77
130.52
129.82
128.16
127.82
125.77
125.74
125.71
125.68
123.00
77.41 cdcl3
76.91 cdcl3
65.59
45.48
40.22
27.58
21.65
f1 (ppm)

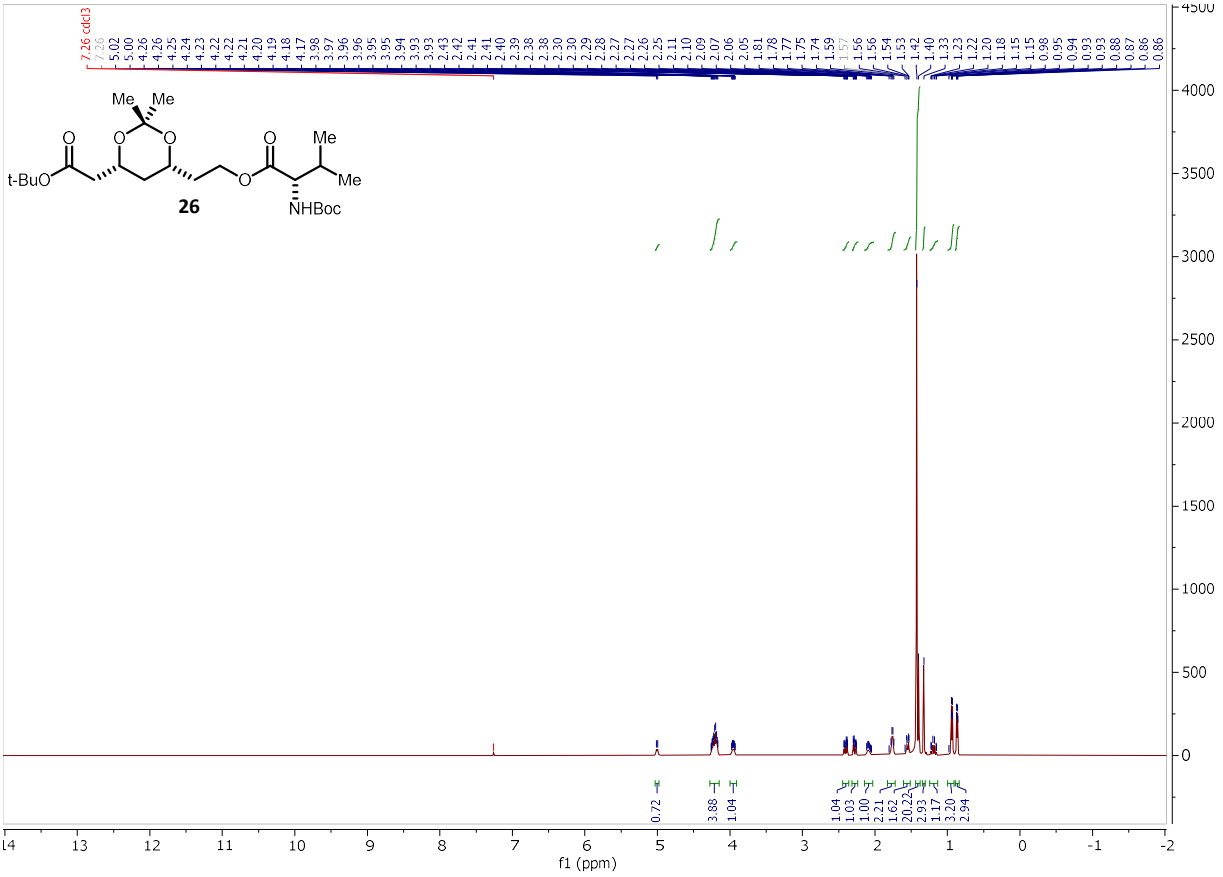

O
O
NTs
F3C
23
-62.67
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

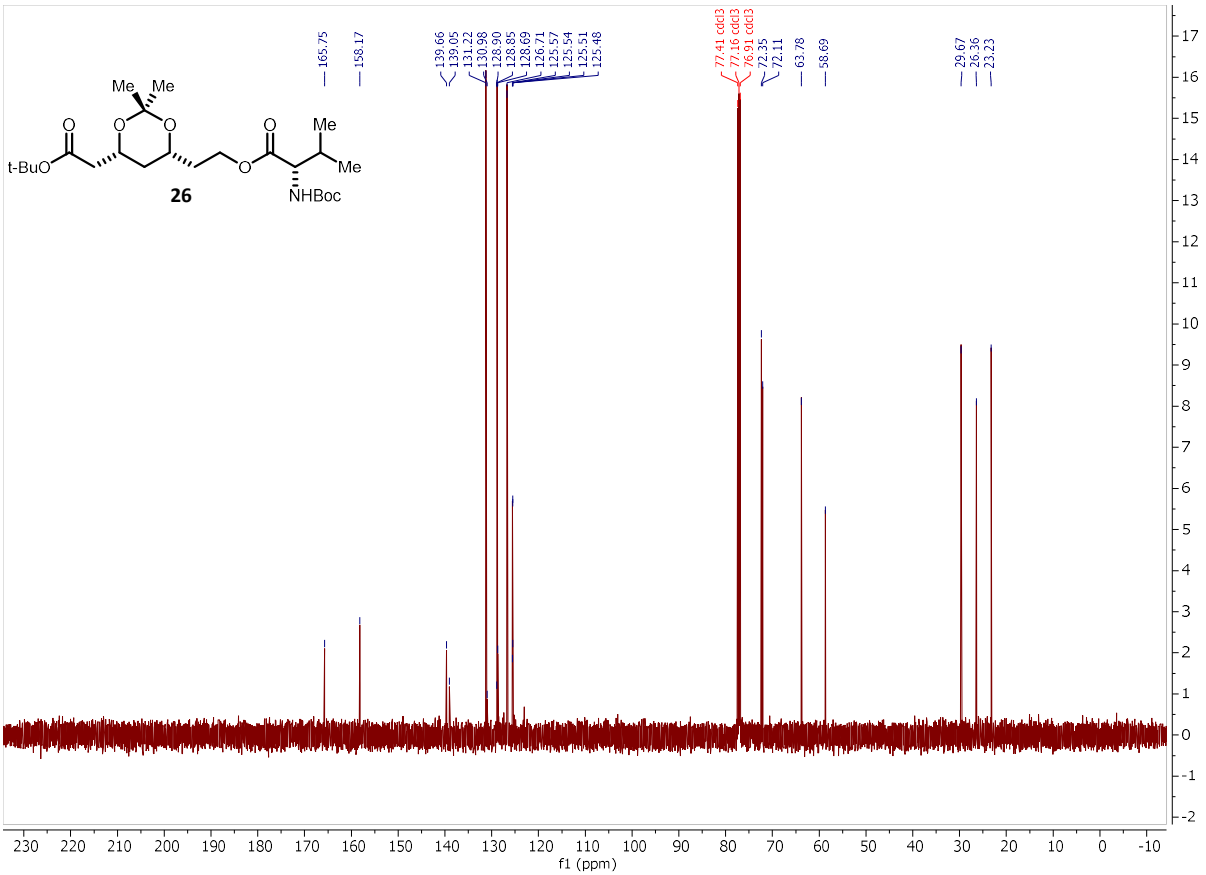

HO
O
O
Cl
24
7.97
7.96
7.96
7.95
7.95
7.95
7.94
7.41
7.41
7.40
7.40
7.39
7.39
7.39
7.26 cdcl3
4.49
4.48
4.47
4.47
4.46
4.46
3.78
3.77
3.76
3.76
3.75
3.75
2.12
2.02
2.02
2.01
2.01
2.00
2.00
1.99
1.98
1.97
1.97
1.82
1.82
2.00
2.00
0.86
2.20
f1 (ppm)

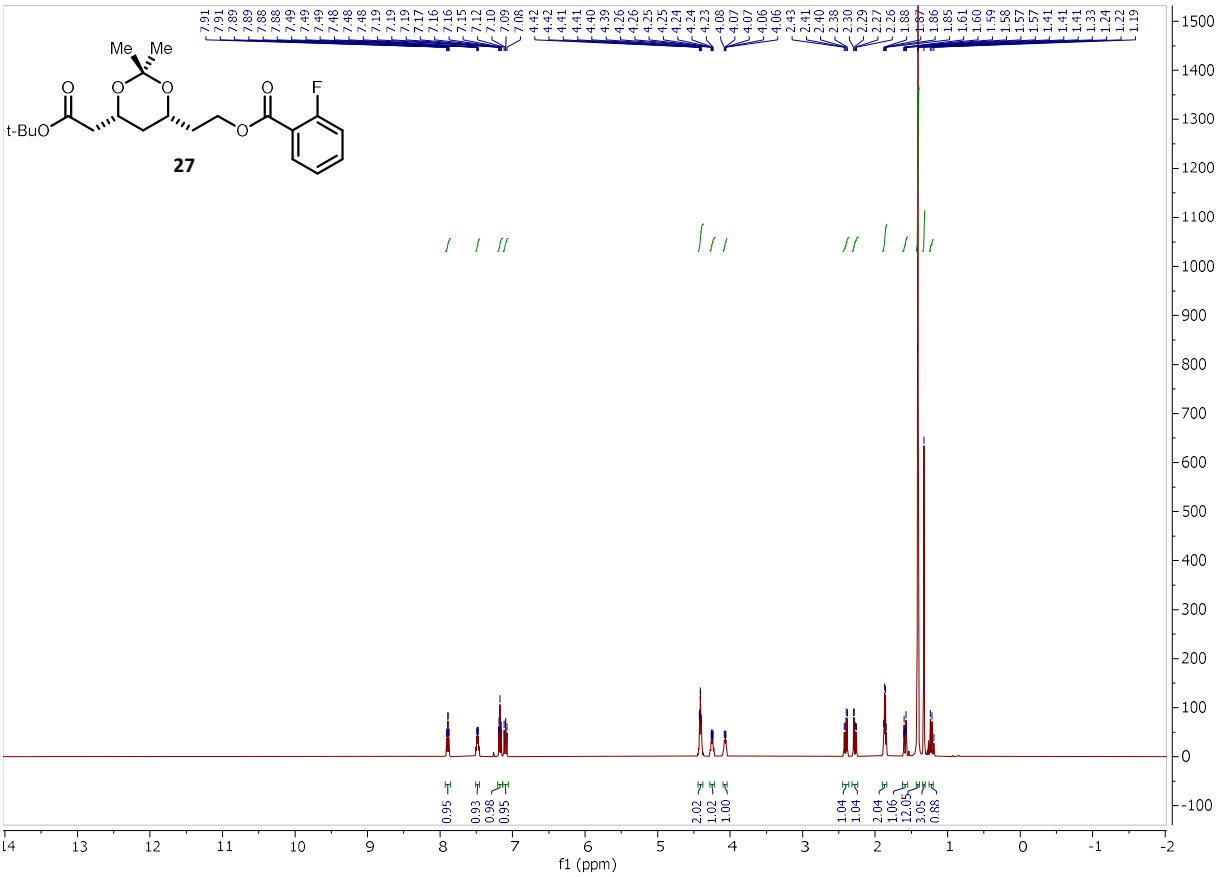

HO
O
O
Cl
24
166.23
139.64
131.11
128.87
128.67
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
62.18
59.23
31.95
f1 (ppm)

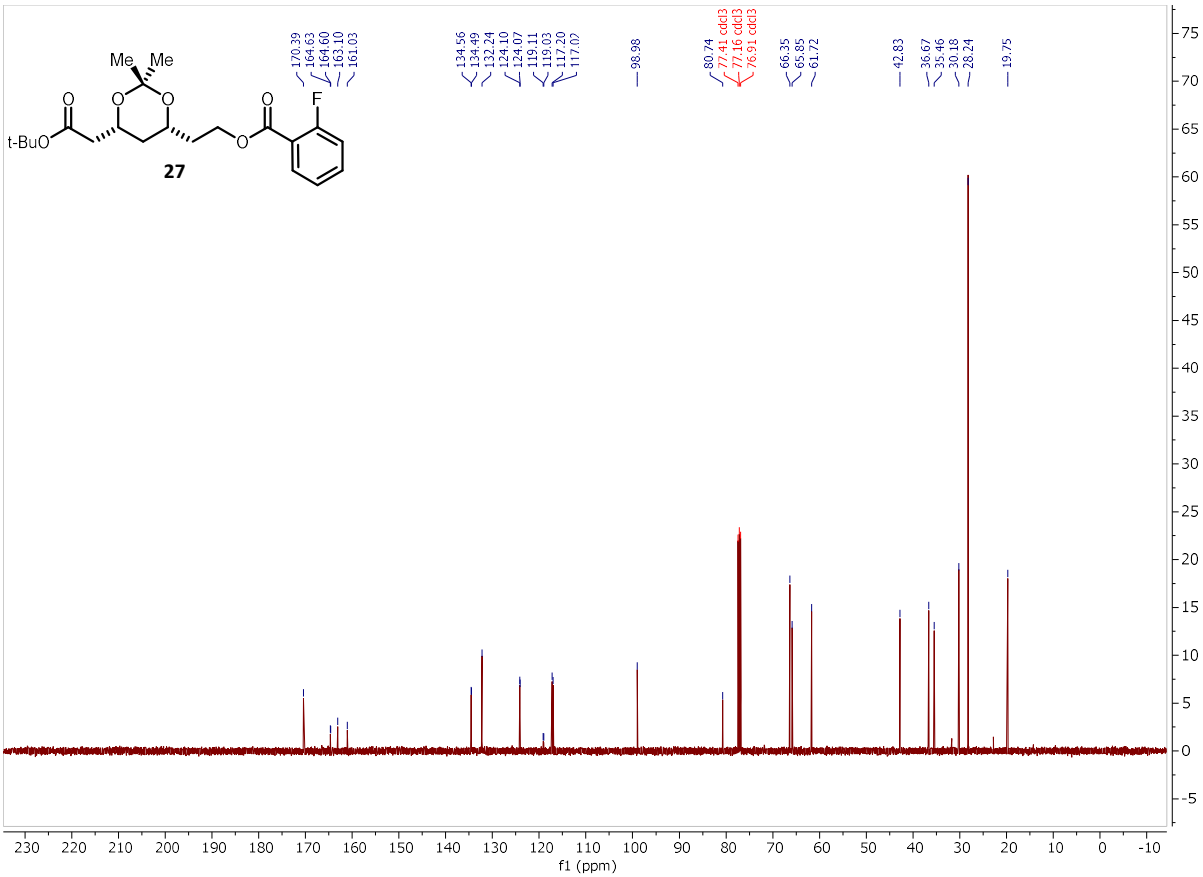

Me
O
O
H
N
O
25
7.26 cdcl3
7.24
7.22
7.16
7.15
6.96
6.89
5.15
5.13
5.10
4.26
4.25
4.24
4.23
2.46
2.45
2.44
2.44
2.43
2.43
2.42
2.41
2.40
2.39
2.37
2.36
2.34 H2O
2.32
2.31
2.30
2.29
2.28
2.27
2.26
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.16
2.15
1.83
1.81
0.91
2.01
0.93
6.31
1.20
f1 (ppm)

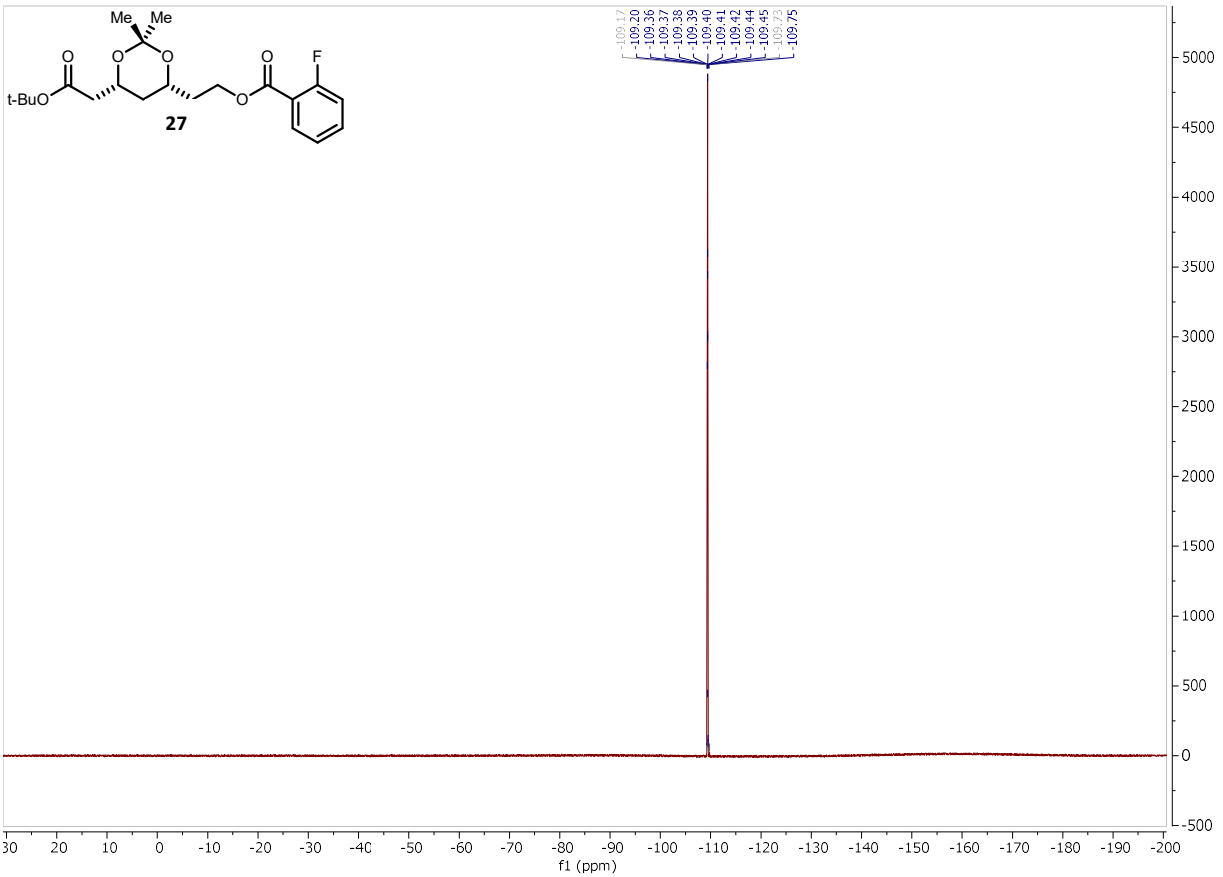

178.21
172.03
138.54
132.20
129.39
128.57
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
67.28
55.58
29.29
24.79
21.24
Me
25
f1 (ppm)

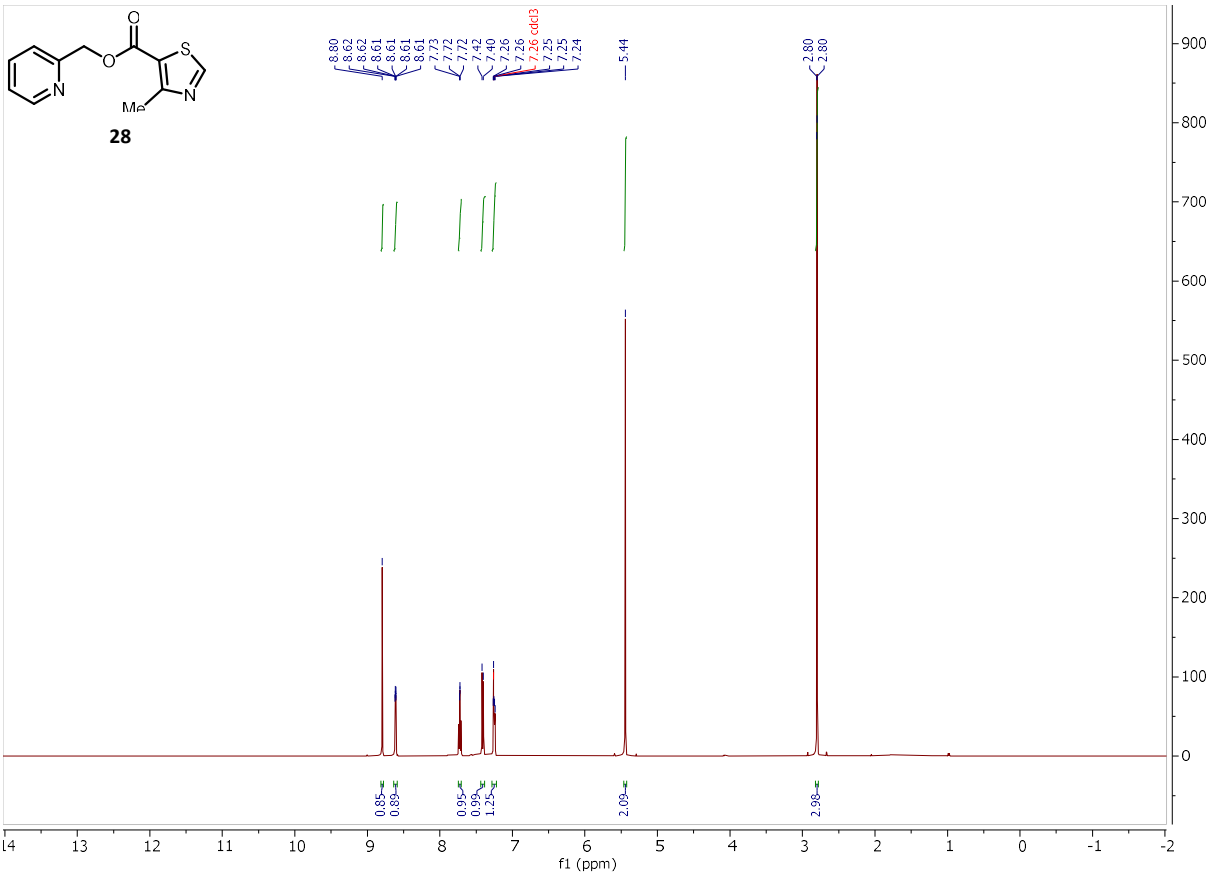

Me
Me
O
O
O
t-BuO
O
O
Me
Me
NHBoc
26
f1 (ppm)

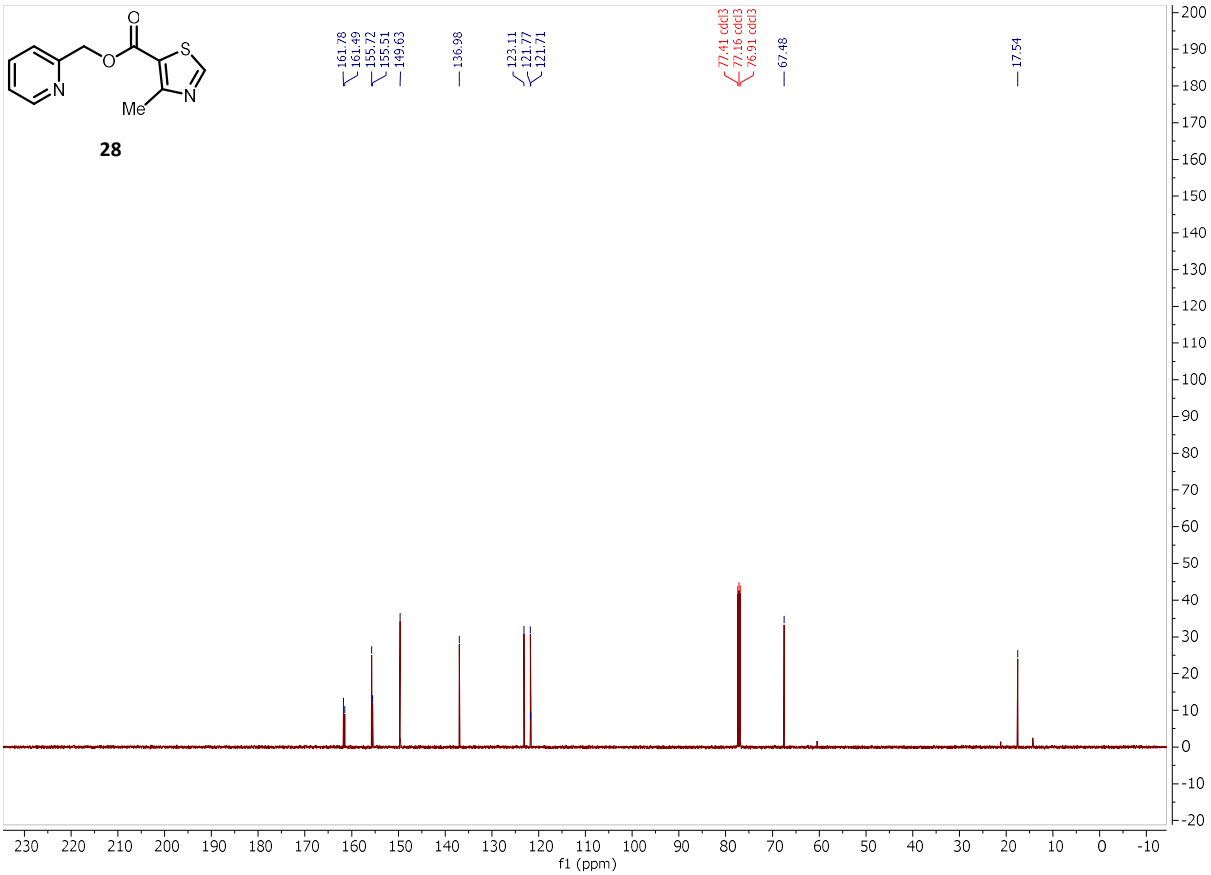

Me
Me
O
O
O
t-BuO
O
Me
Me
NHBoc
26
165.75
158.17
139.66
139.05
131.22
130.98
128.90
128.85
128.69
126.71
125.57
125.54
125.51
125.48
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
72.35
72.11
63.78
58.69
29.67
26.36
23.23
f1 (ppm)

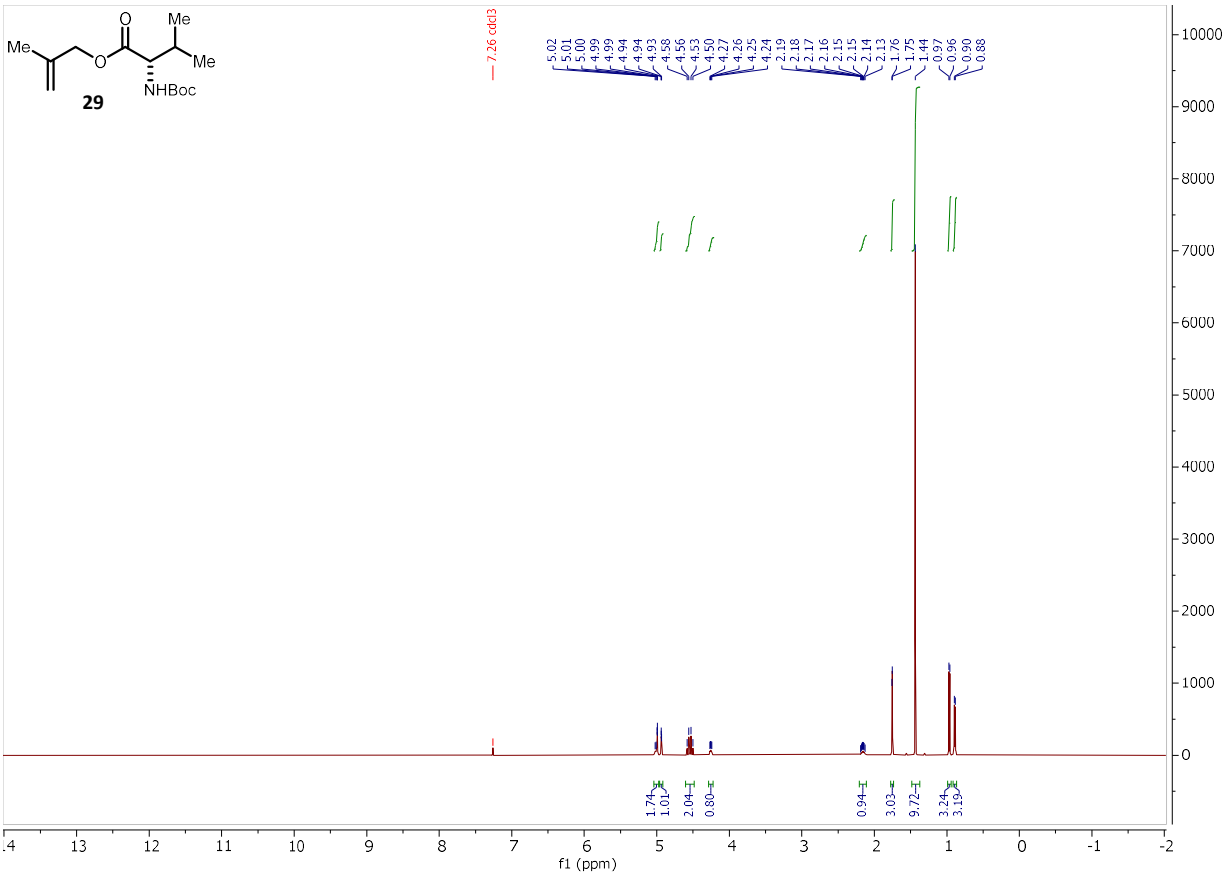

Me
Me
O
O
O
O
O
F
t-BuO
27
f1 (ppm)

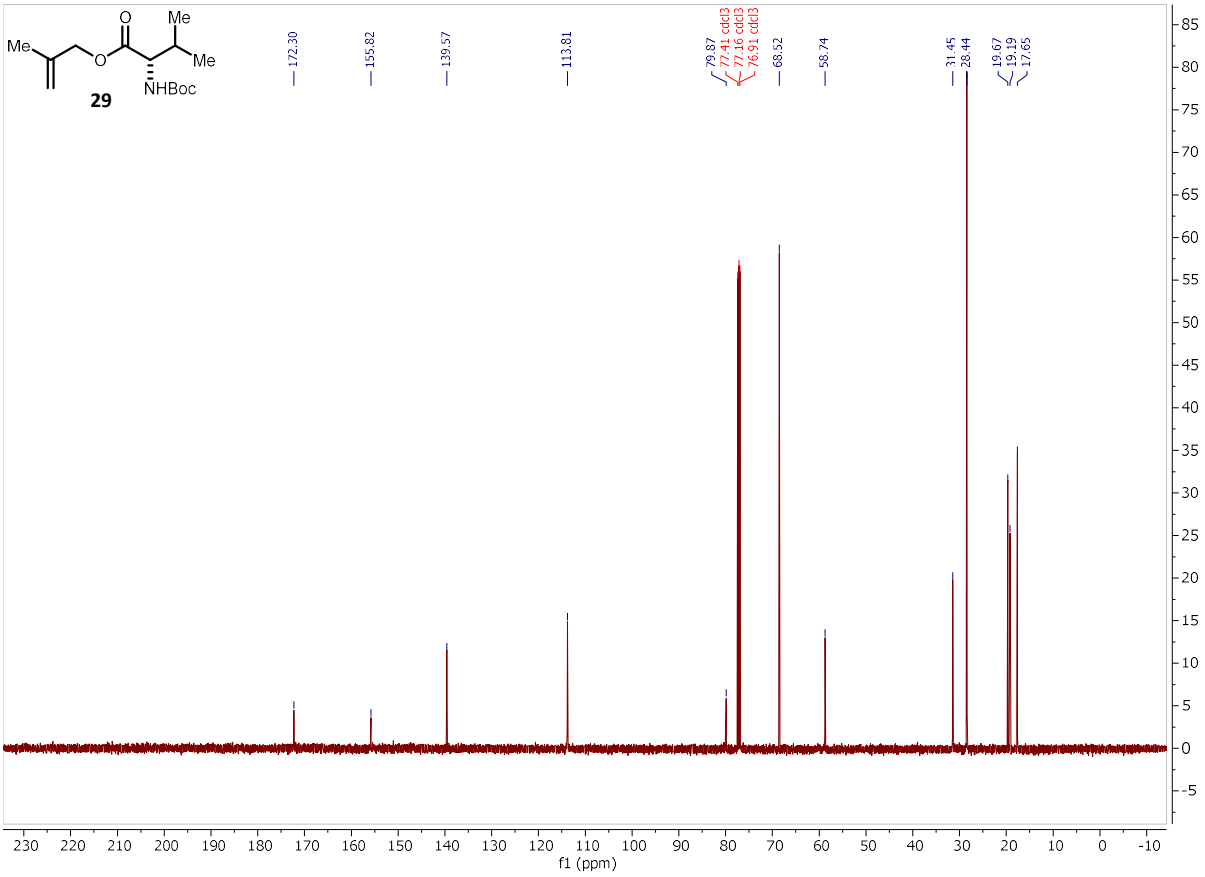

Me
Me
O
O
O
t-BuO
O
O
F
27
170.39
164.63
164.60
163.10
161.03
134.56
134.49
132.24
124.10
124.07
119.11
119.03
117.20
117.07
98.98
80.74
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
66.35
65.85
61.72
42.83
36.67
35.46
30.18
28.24
19.75
f1 (ppm)

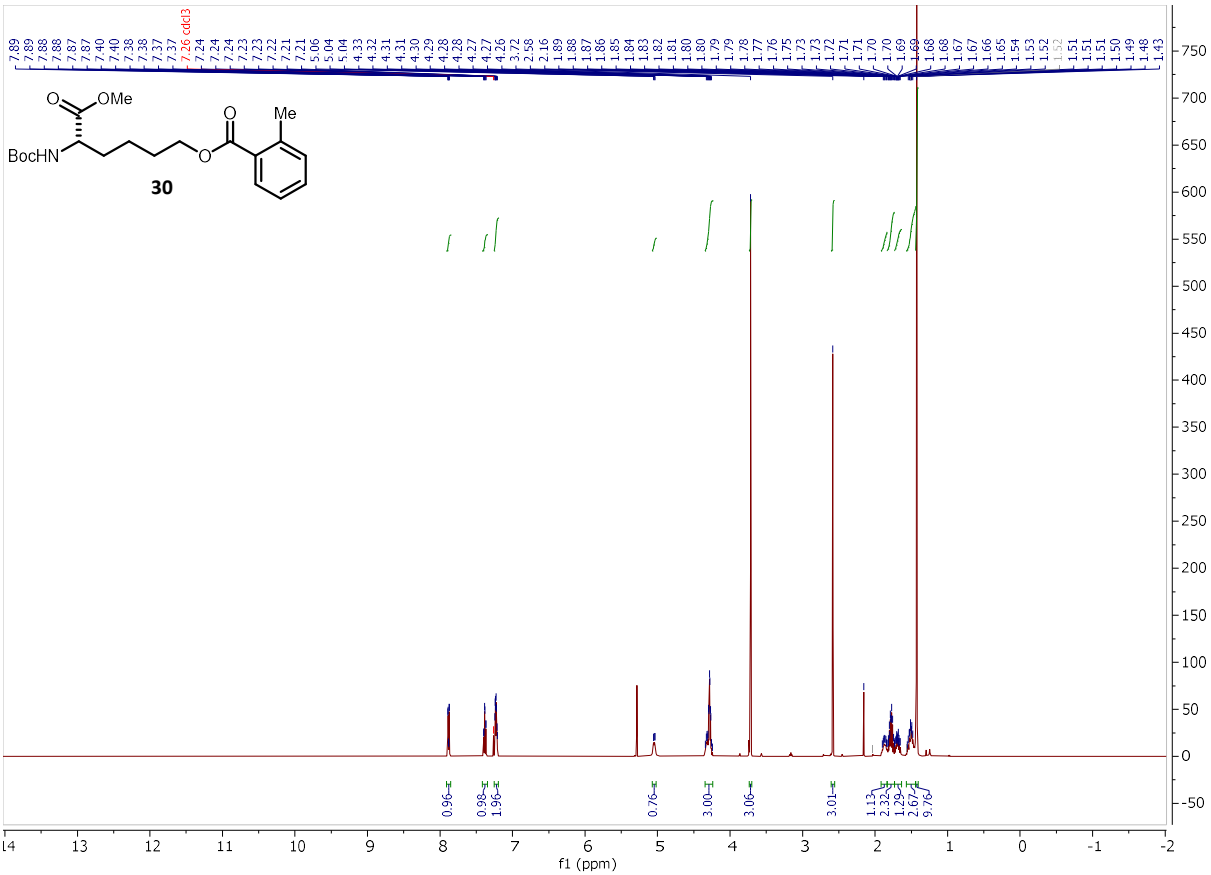

Me
Me
O
O
O
O
O
F
t-BuO
27
-109.17
-109.20
-109.36
-109.37
-109.38
-109.39
-109.40
-109.41
-109.42
-109.44
-109.45
-109.73
-109.75
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

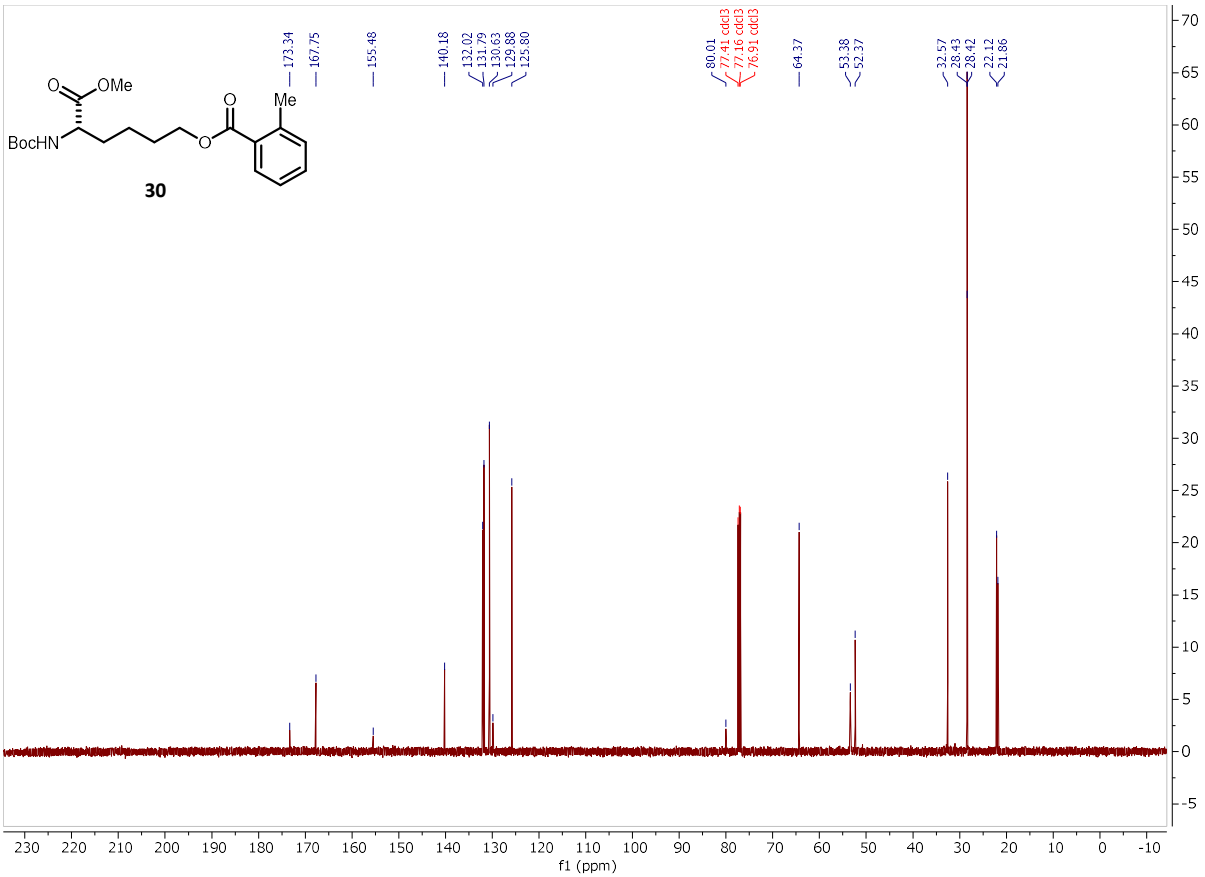

28
8.80
8.62
8.62
8.61
8.61
8.61
8.61
7.73
7.72
7.72
7.42
7.40
7.26
7.26
7.26 cdcl3
7.25
7.25
7.24
5.44
2.80
2.80
0.85
0.89
0.95
0.99
1.25
2.09
2.98
f1 (ppm)

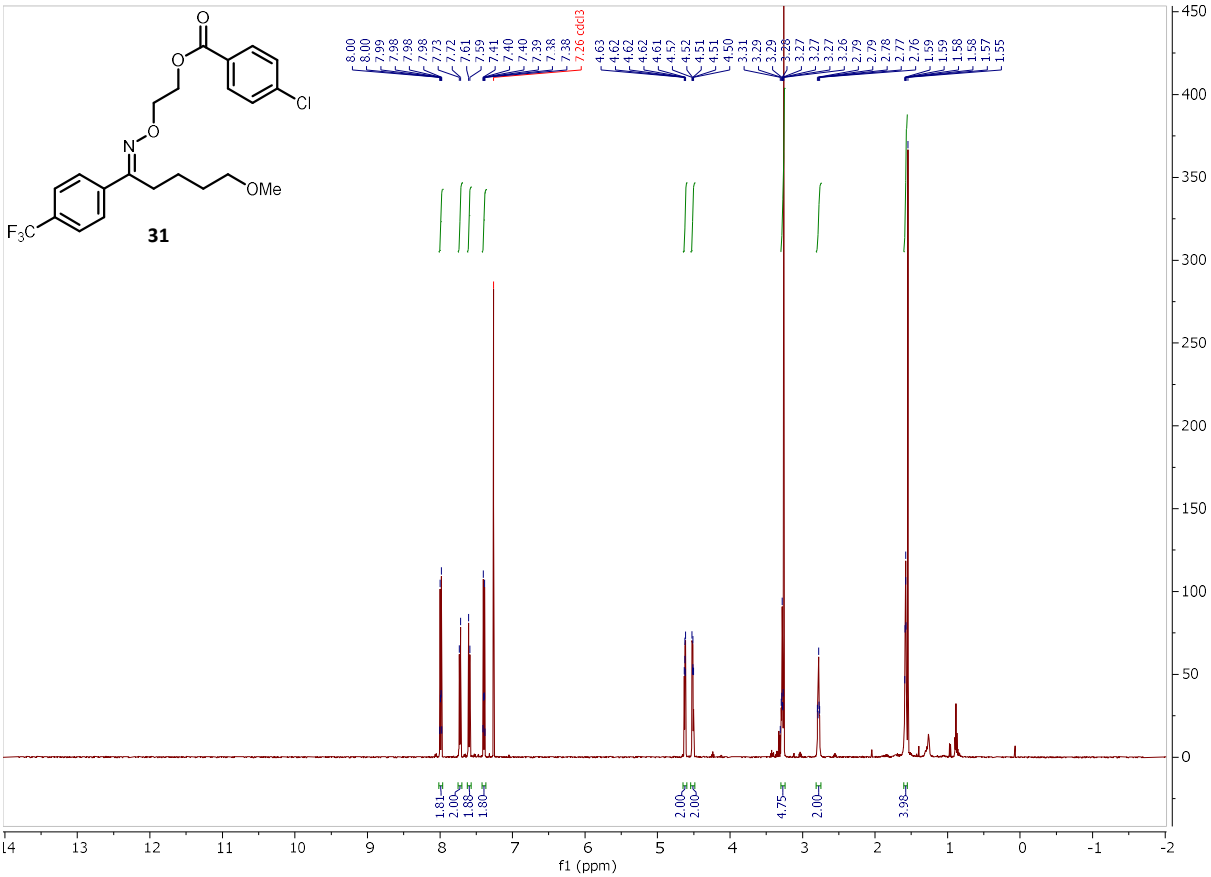

28
161.78
161.49
155.72
155.51
149.63
136.98
123.11
121.77
121.71
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
67.48
17.54
f1 (ppm)

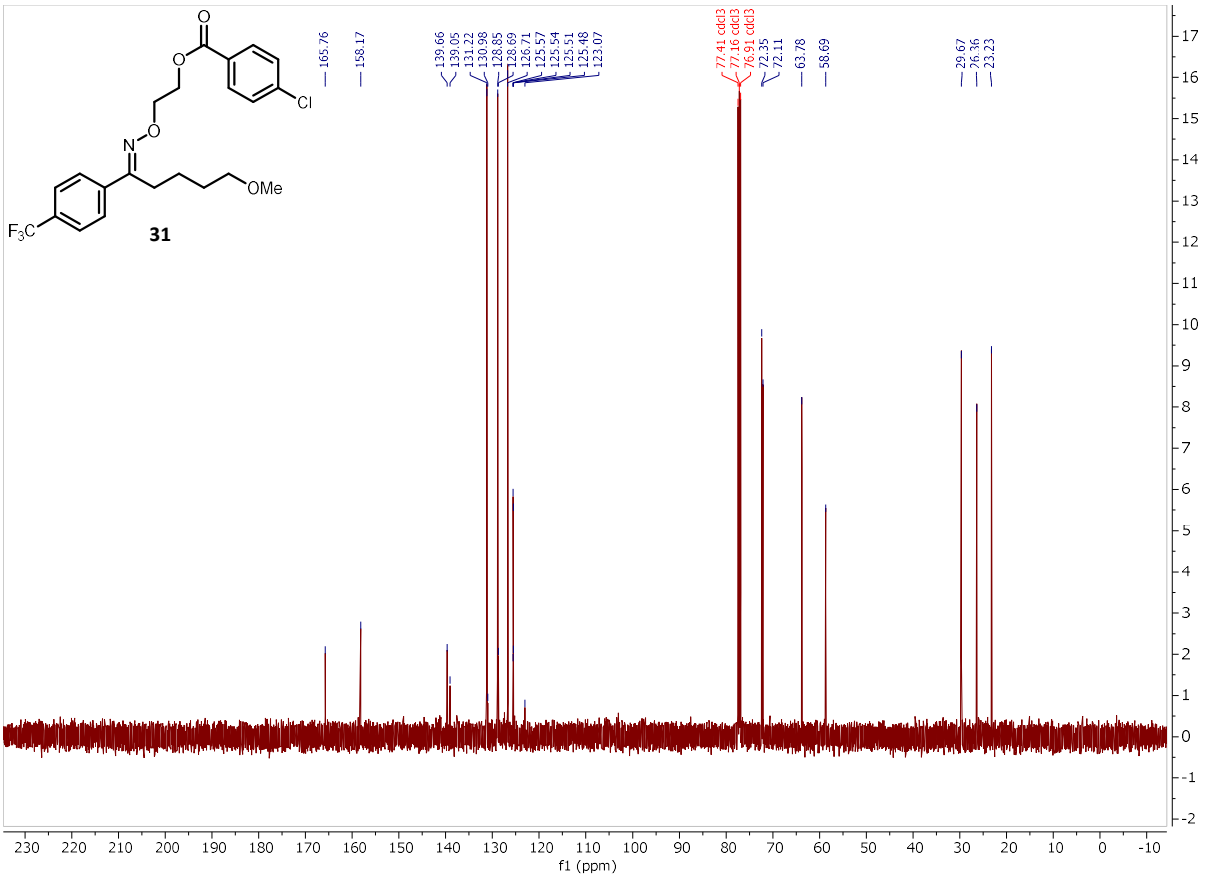

Me
O
Me
Me
O
NHBoc
29
7.26 cdcl3
5.02
5.01
5.00
4.99
4.99
4.94
4.94
4.93
4.58
4.56
4.53
4.50
4.27
4.26
4.25
4.24
2.19
2.18
2.17
2.16
2.15
2.15
2.14
2.13
1.76
1.75
1.44
0.97
0.96
0.90
0.88
1.74
1.01
2.04
0.80
0.94
3.03
9.72
3.24
3.19
f1 (ppm)

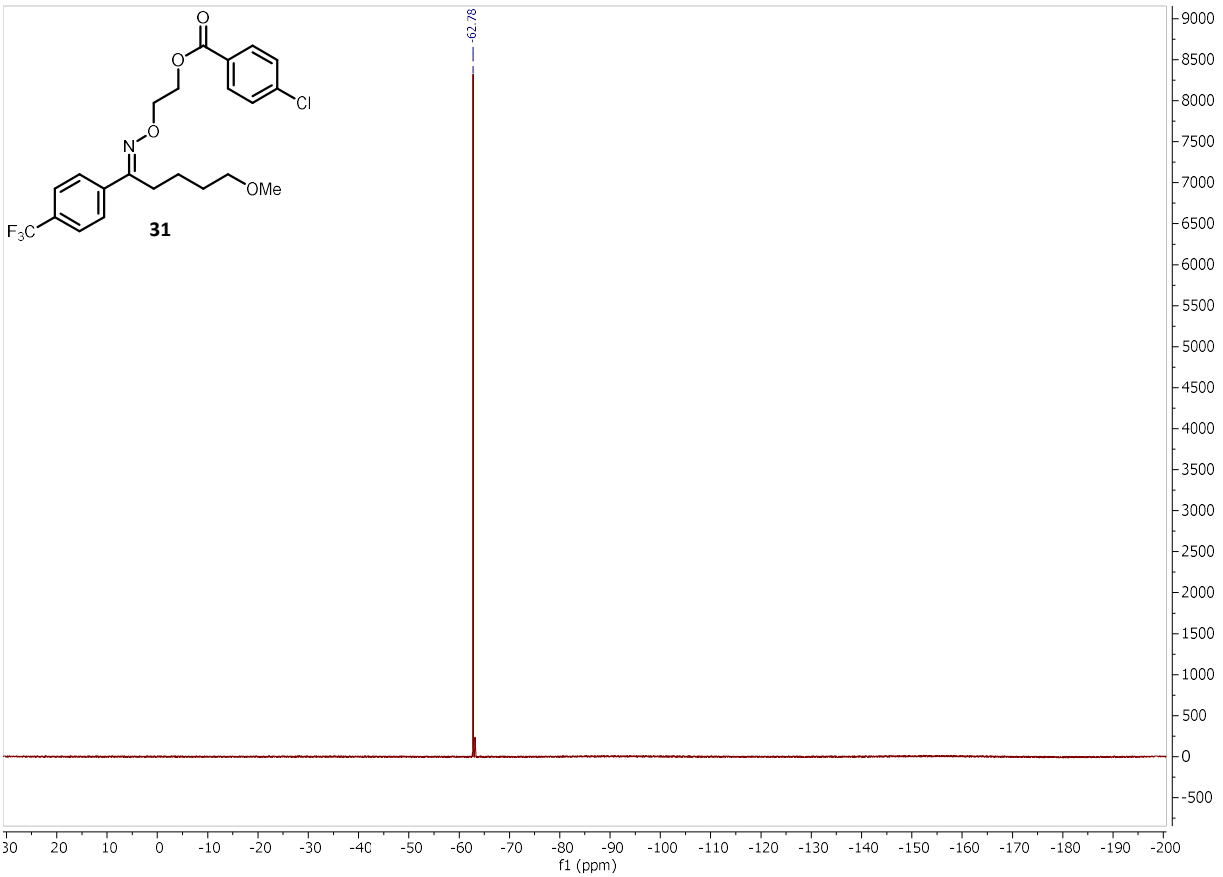

29
172.30
155.82
139.57
113.81
79.87
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
68.52
58.74
31.45
28.44
19.67
19.19
17.65
f1 (ppm)

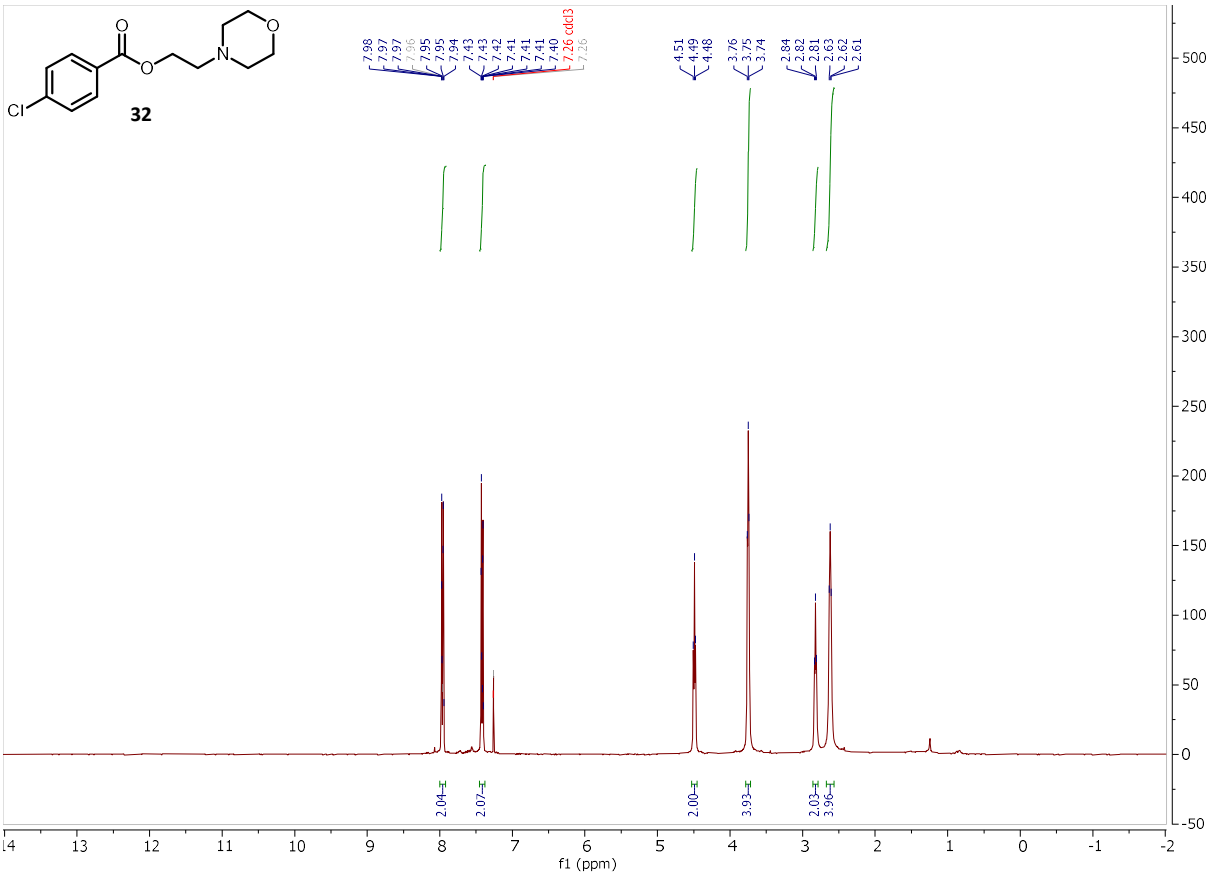

O
OMe
BocHN
O
O
Me
30
f1 (ppm)

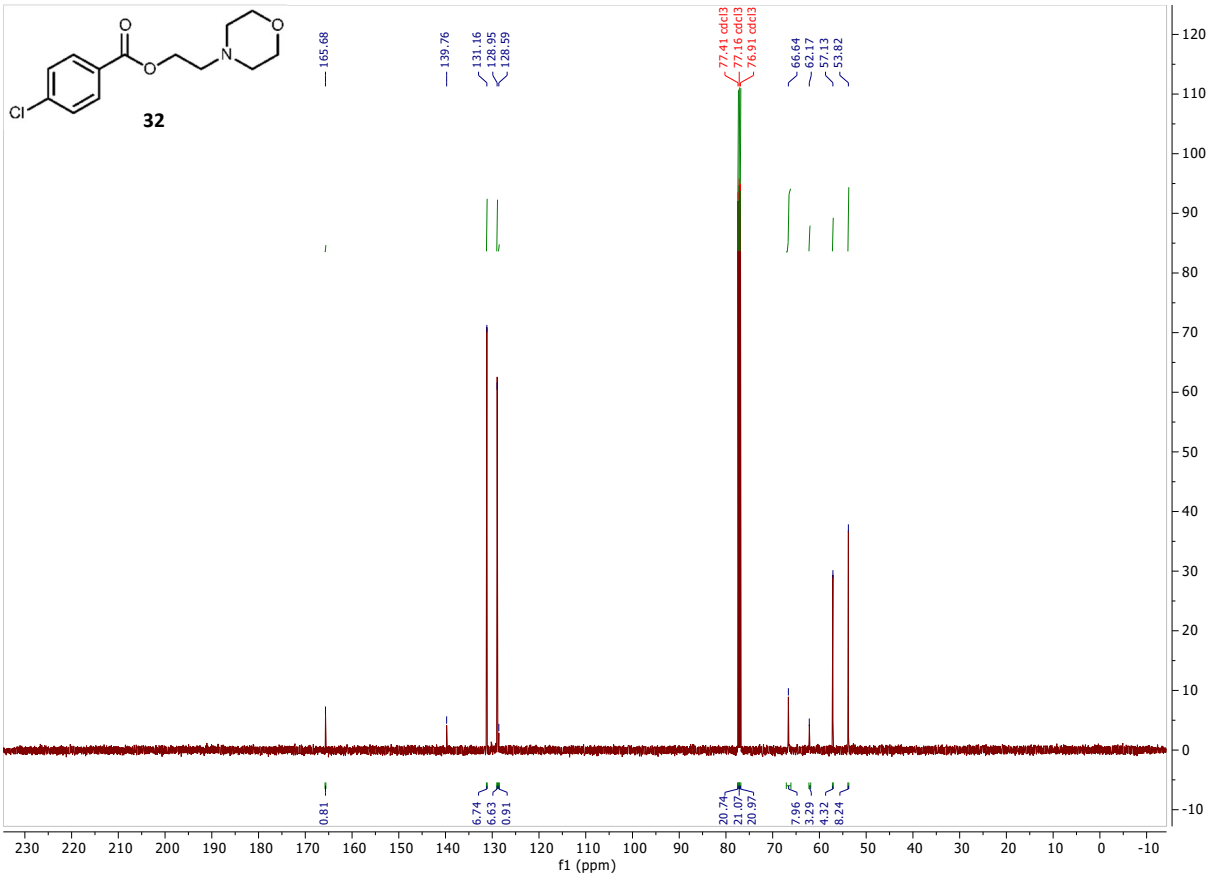

30
173.34
167.75
155.48
140.18
132.02
131.76
130.63
129.88
125.80
80.01
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
64.37
53.38
52.37
32.57
28.43
28.42
22.12
21.86
f1 (ppm)

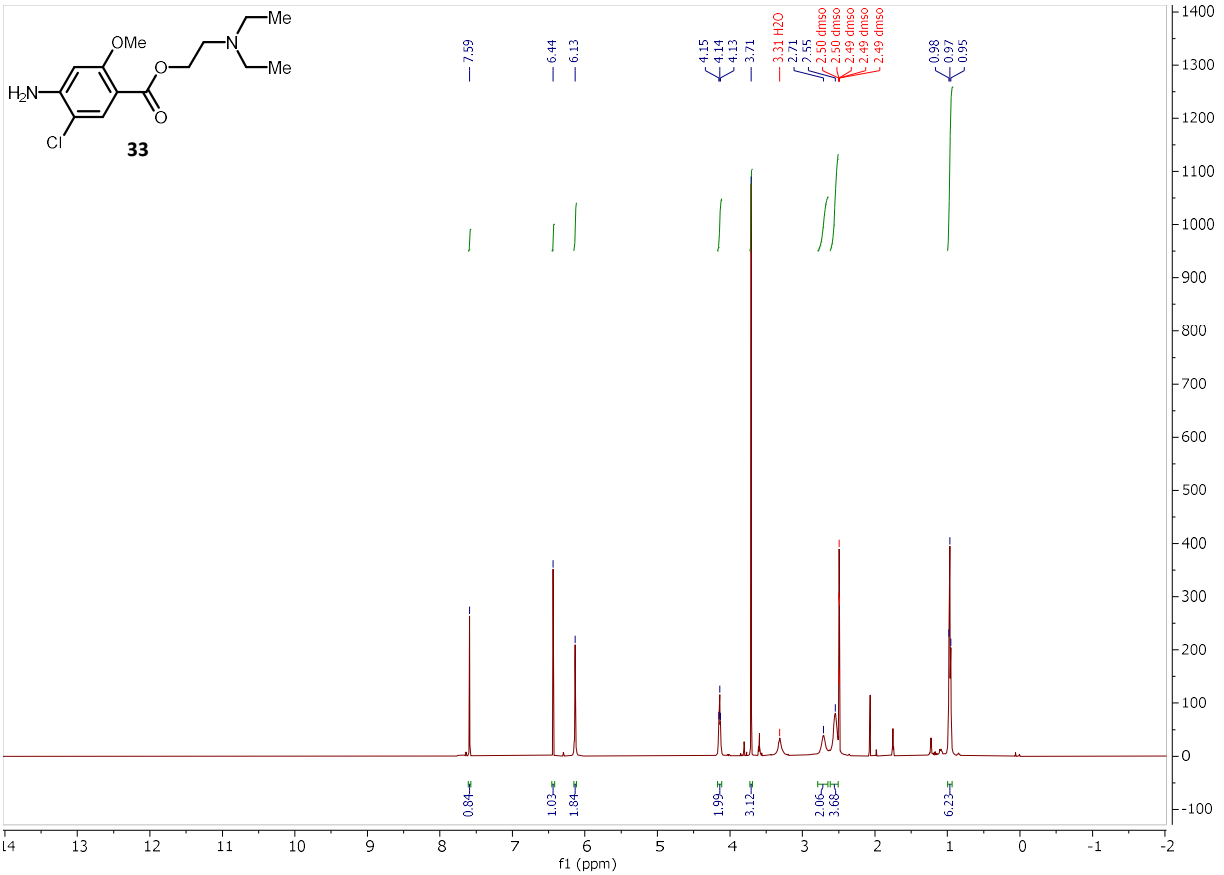

O
O
Cl
N
O
OMe
F3C
31
f1 (ppm)

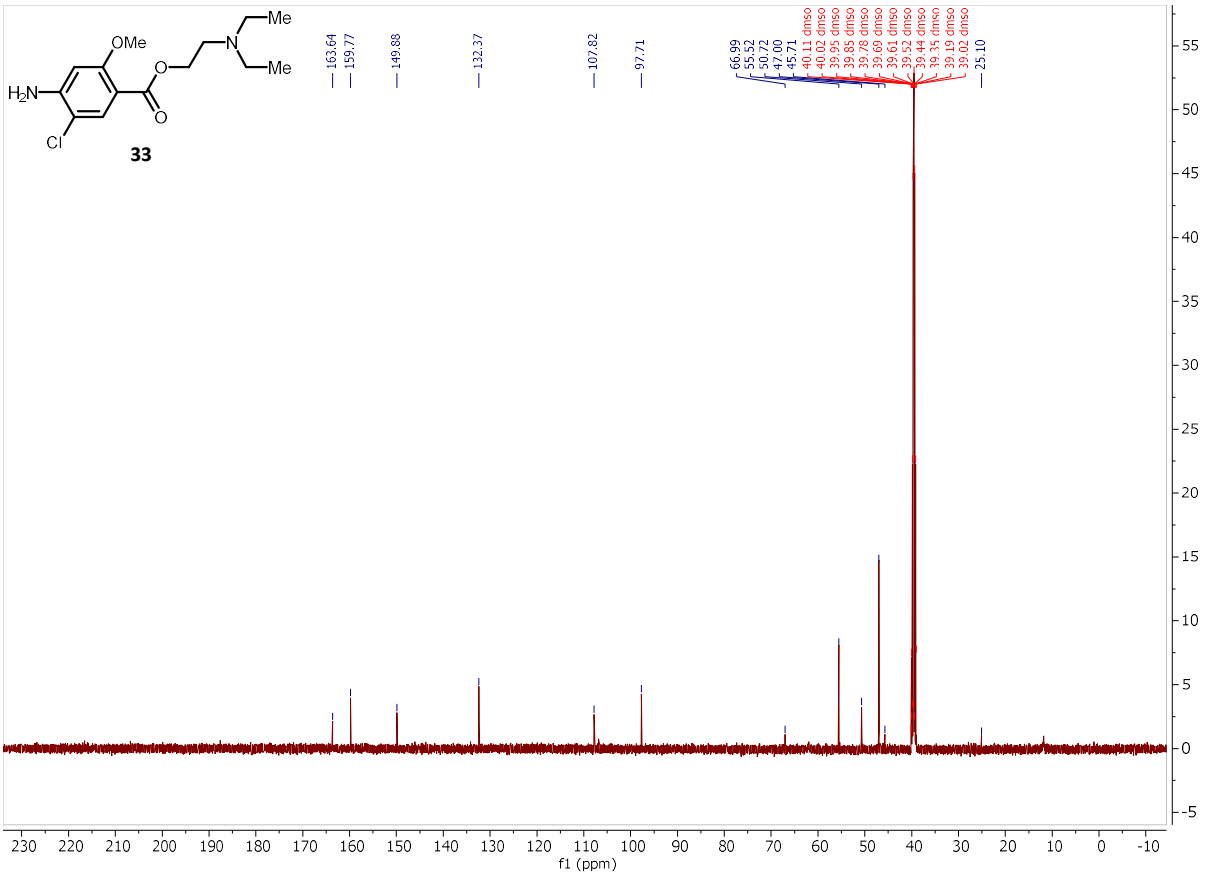

31
165.76
158.17
139.66
139.05
131.22
130.98
128.85
128.69
126.71
125.57
125.54
125.51
125.48
123.07
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
72.35
72.11
63.78
58.69
29.67
26.36
23.23
f1 (ppm)

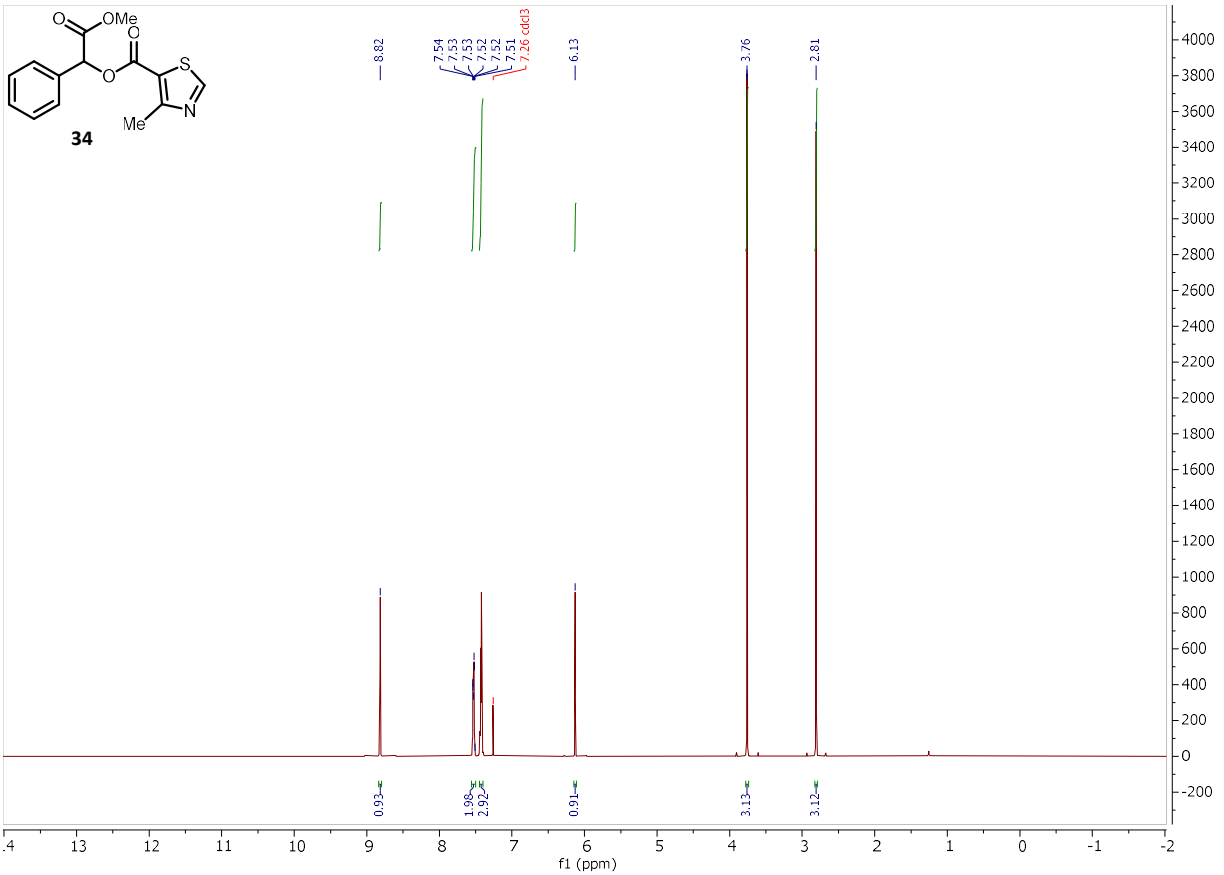

-62.78
O
O
Cl
N
O
OMe
F3C
31
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

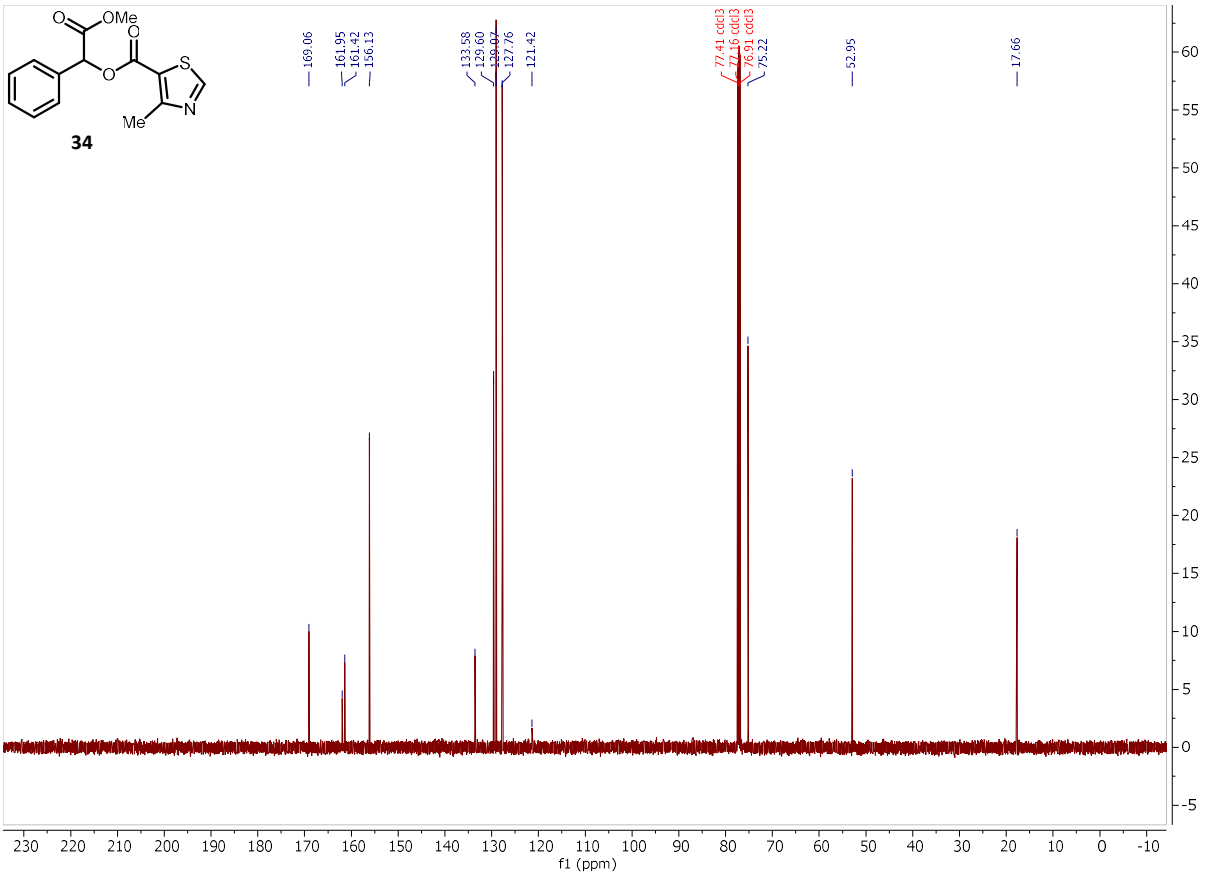

32
7.98
7.97
7.97
7.96
7.95
7.95
7.94
7.43
7.43
7.42
7.41
7.41
7.41
7.40
7.26 cdcl3
7.26
4.51
4.49
4.48
3.76
3.75
3.74
2.84
2.82
2.81
2.63
2.62
2.61
2.04
2.07
2.00
3.93
2.03
3.96
f1 (ppm)

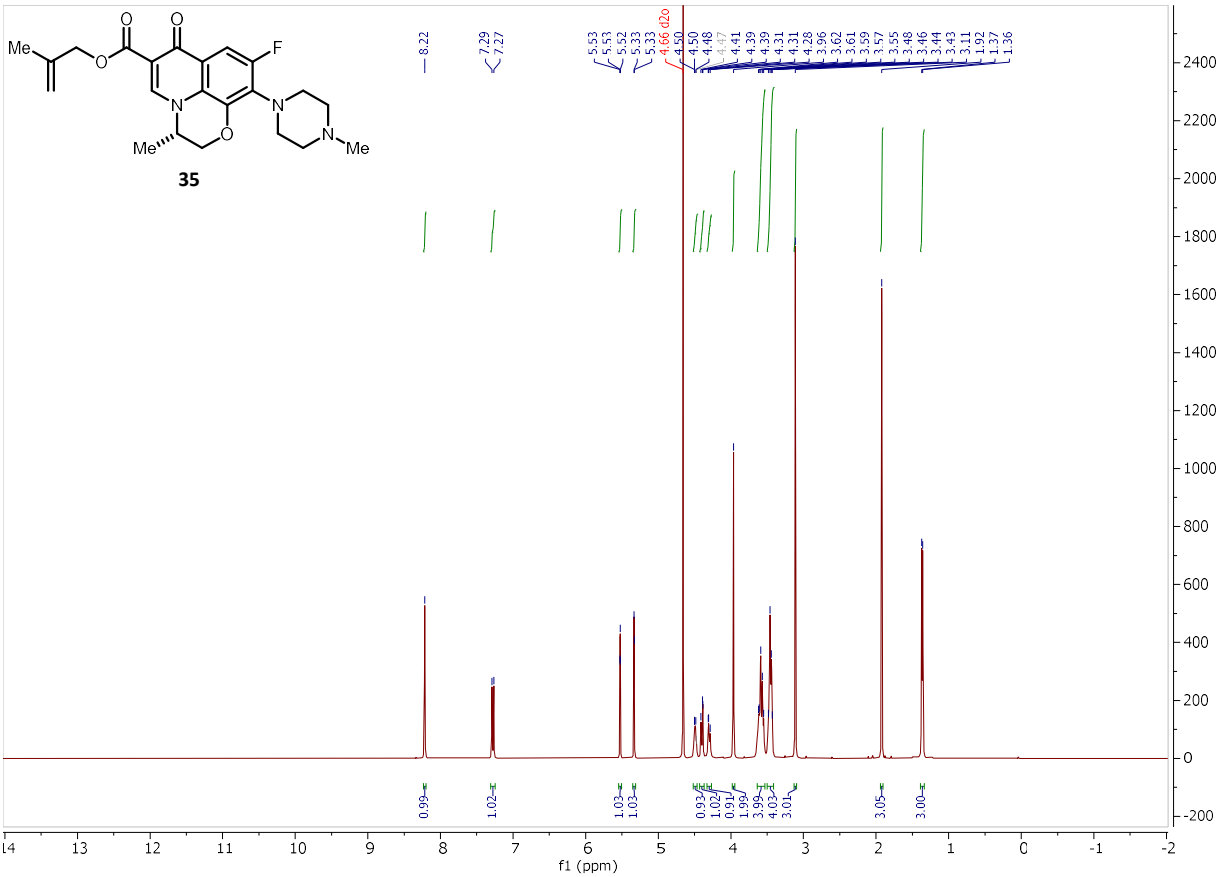

32
165.68
139.76
131.16
128.95
128.59
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
66.64
62.17
57.13
53.82
0.81
6.74
6.63
0.91
20.74
21.07
20.97
7.96
3.29
4.32
8.24
f1 (ppm)

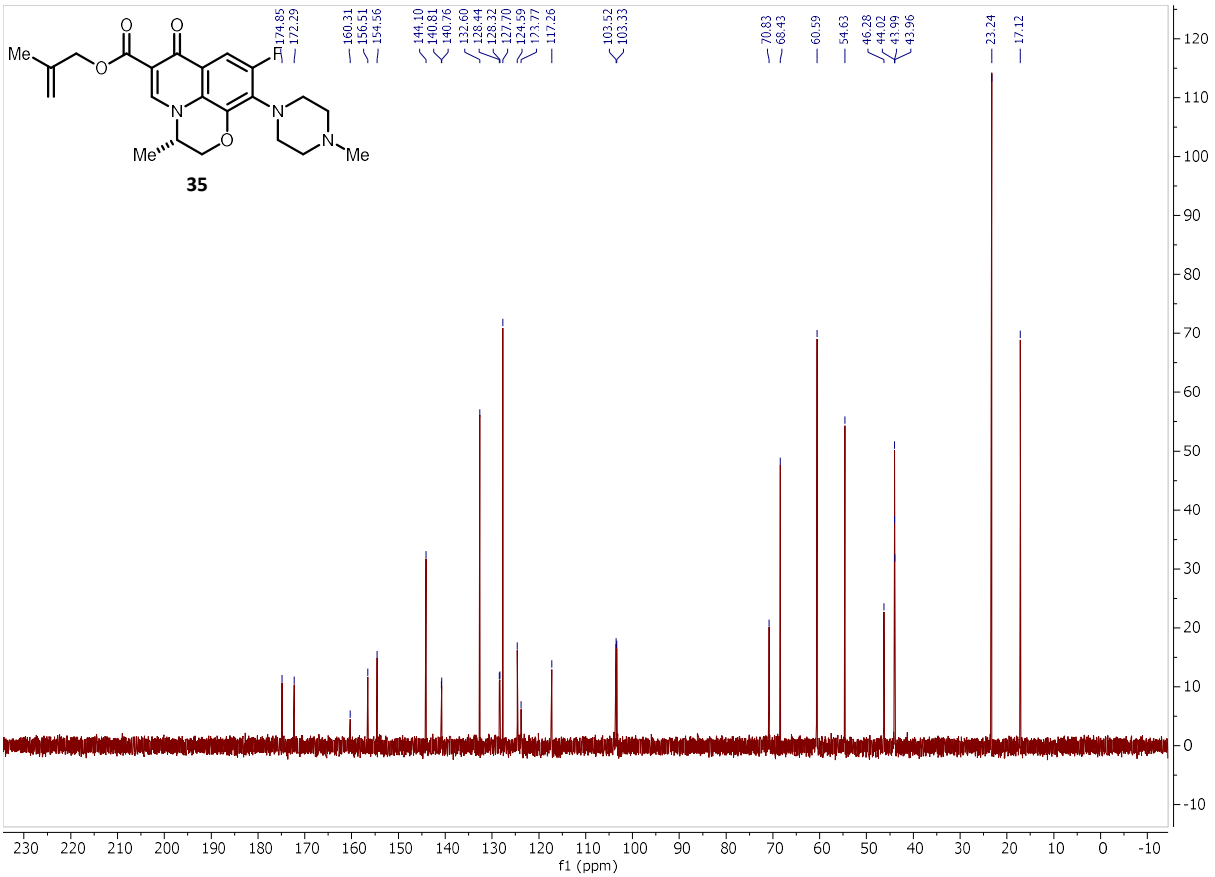

OMe
Me
N
Me
O
H2N
O
Cl
33
7.59
6.44
6.13
4.15
4.14
4.13
3.71
3.31 H2O
2.71
2.55
2.50 dmso
2.50 dmso
2.49 dmso
2.49 dmso
2.49 dmso
0.98
0.97
0.95
0.84
1.03
1.84
1.99
3.12
2.06
3.68
6.23
f1 (ppm)

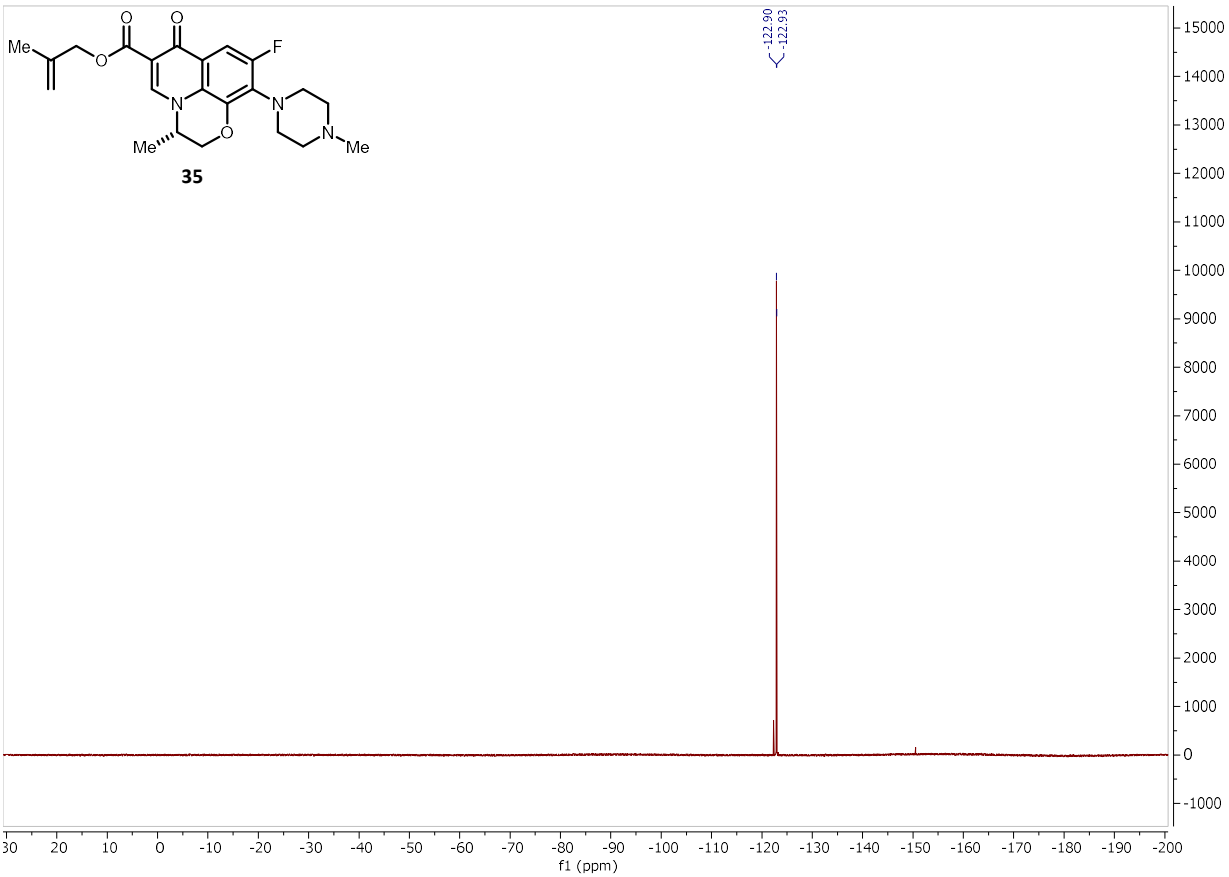

OMe
Me
N
Me
O
H2N
O
Cl
33
163.64
159.77
149.88
132.37
107.82
97.71
66.99
55.52
50.72
47.00
45.71
40.11 dmso
40.02 dmso
39.95 dmso
39.85 dmso
39.78 dmso
39.69 dmso
39.61 dmso
39.52 dmso
39.44 dmso
39.35 dmso
39.19 dmso
39.02 dmso
25.10
f1 (ppm)

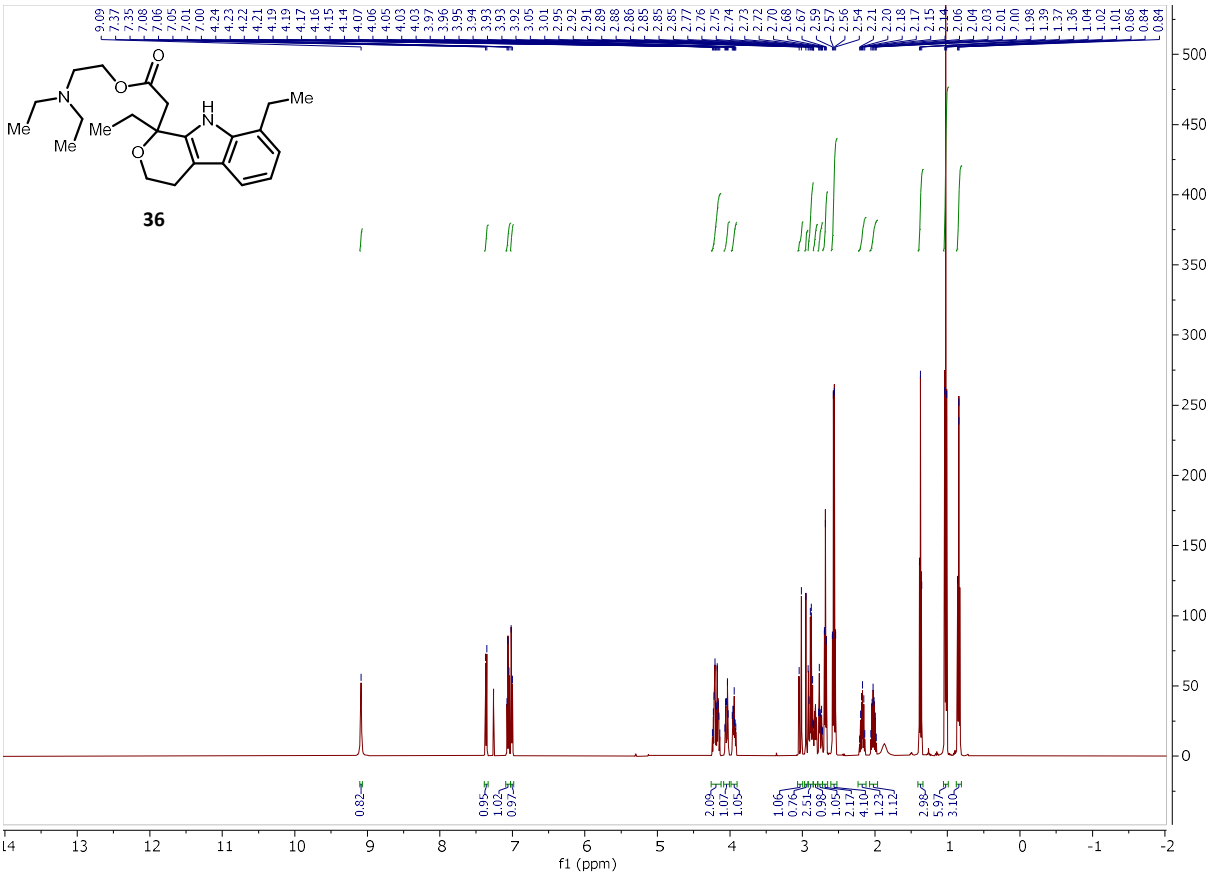

OMe
O
O
O
S
N
Me
34
8.82
7.54
7.53
7.53
7.52
7.52
7.51
7.26 cdcl3
6.13
3.76
2.81
0.93
1.98
2.92
0.91
3.13
3.12
f1 (ppm)

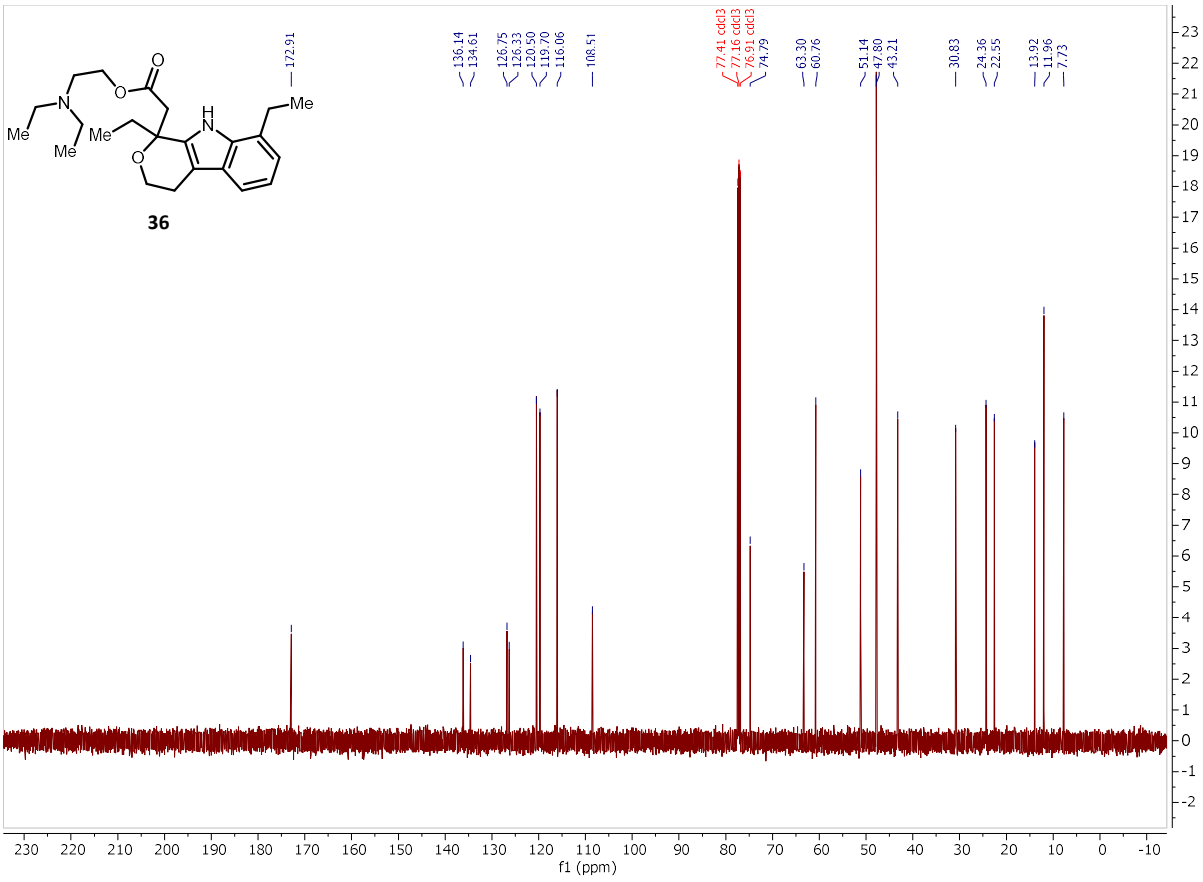

OMe
O
O
O
S
N
Me
34
169.06
161.95
161.42
156.13
133.58
129.60
130.07
127.76
121.42
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
75.22
52.95
17.66
f1 (ppm)


35
8.22
7.29
7.27
5.53
5.53
5.52
5.33
5.33
4.66
4.50
4.50
4.48
4.41
4.39
4.39
4.31
4.31
4.28
3.96
3.62
3.61
3.59
3.57
3.55
3.48
3.46
3.44
3.43
3.11
1.92
1.37
1.36
0.99
1.02
1.03
1.03
0.93
1.02
0.91
1.99
3.99
4.03
3.01
3.05
3.00
f1 (ppm)

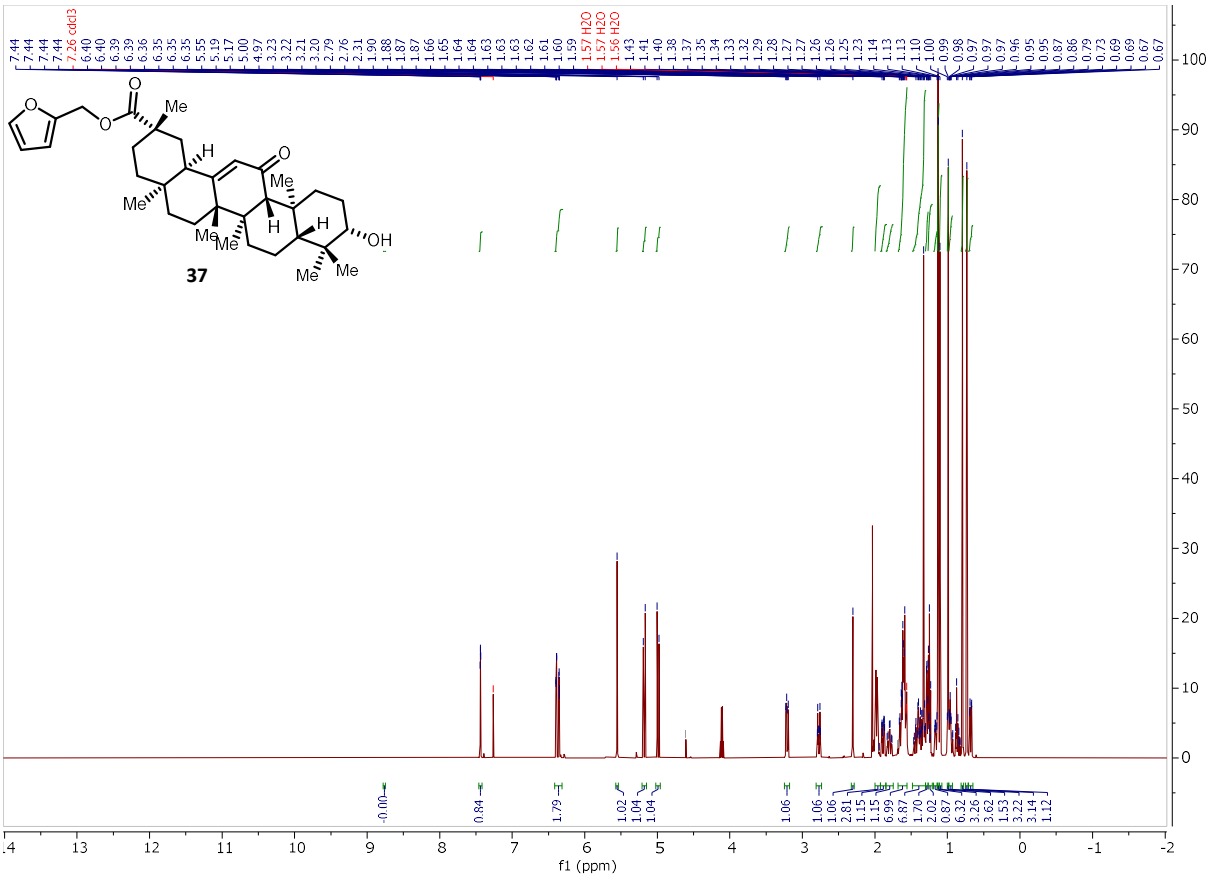

35
174.85
172.29
160.31
156.51
154.56
144.10
140.81
140.76
132.60
128.44
128.32
127.70
124.59
123.77
117.26
103.52
103.33
70.83
68.43
60.59
54.63
46.28
44.02
43.99
43.96
23.24
17.12
f1 (ppm)

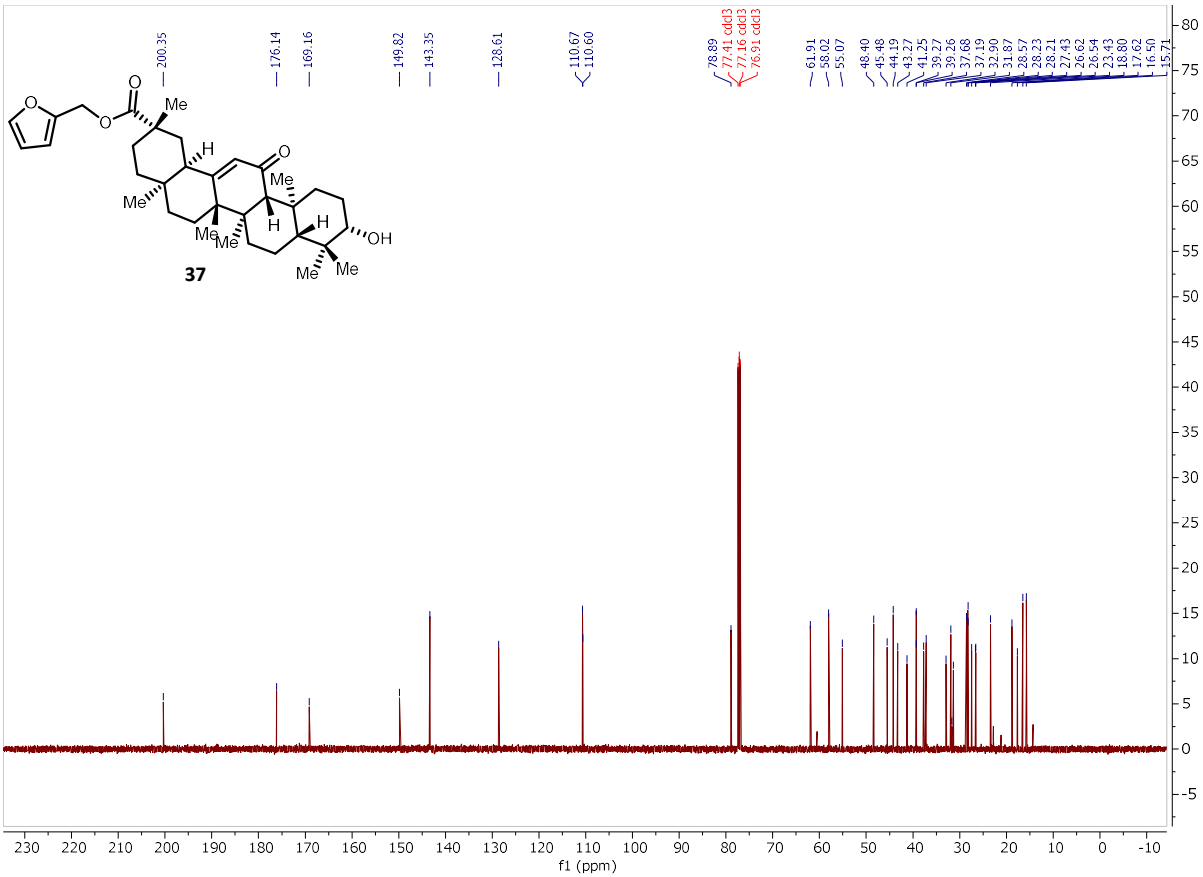

Me
O
O
O
F
N
N
Me
O
N
Me
35
-122.90
-122.93
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)


Me
Me
Me
N
O
O
O
H
N
Me
36
f1 (ppm)

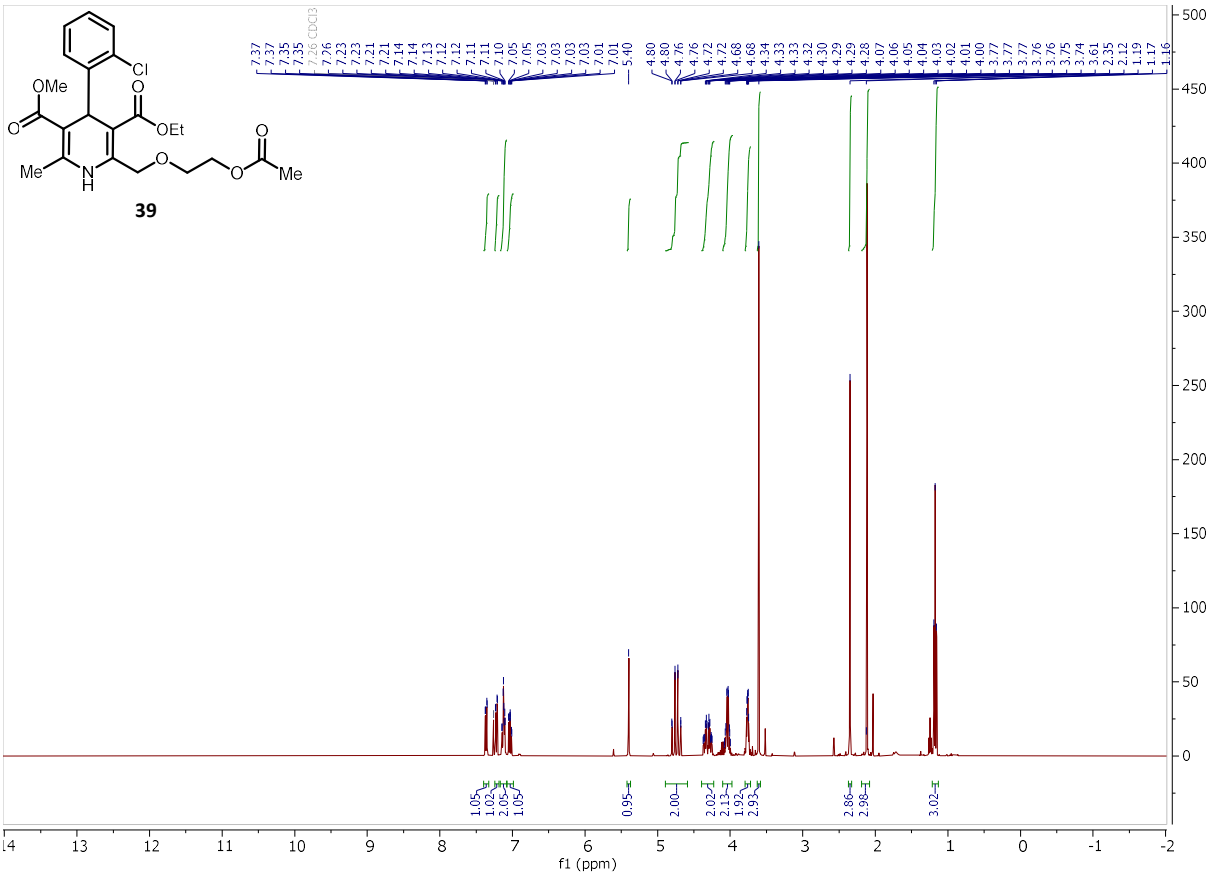

172.91
136.14
134.61
126.75
126.33
120.50
119.70
116.06
108.51
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
74.79
63.30
60.76
51.14
47.80
43.21
30.83
24.36
22.55
13.92
11.96
7.73
Me
Me
Me
Me
O
O
O
N
H
N
f1 (ppm)

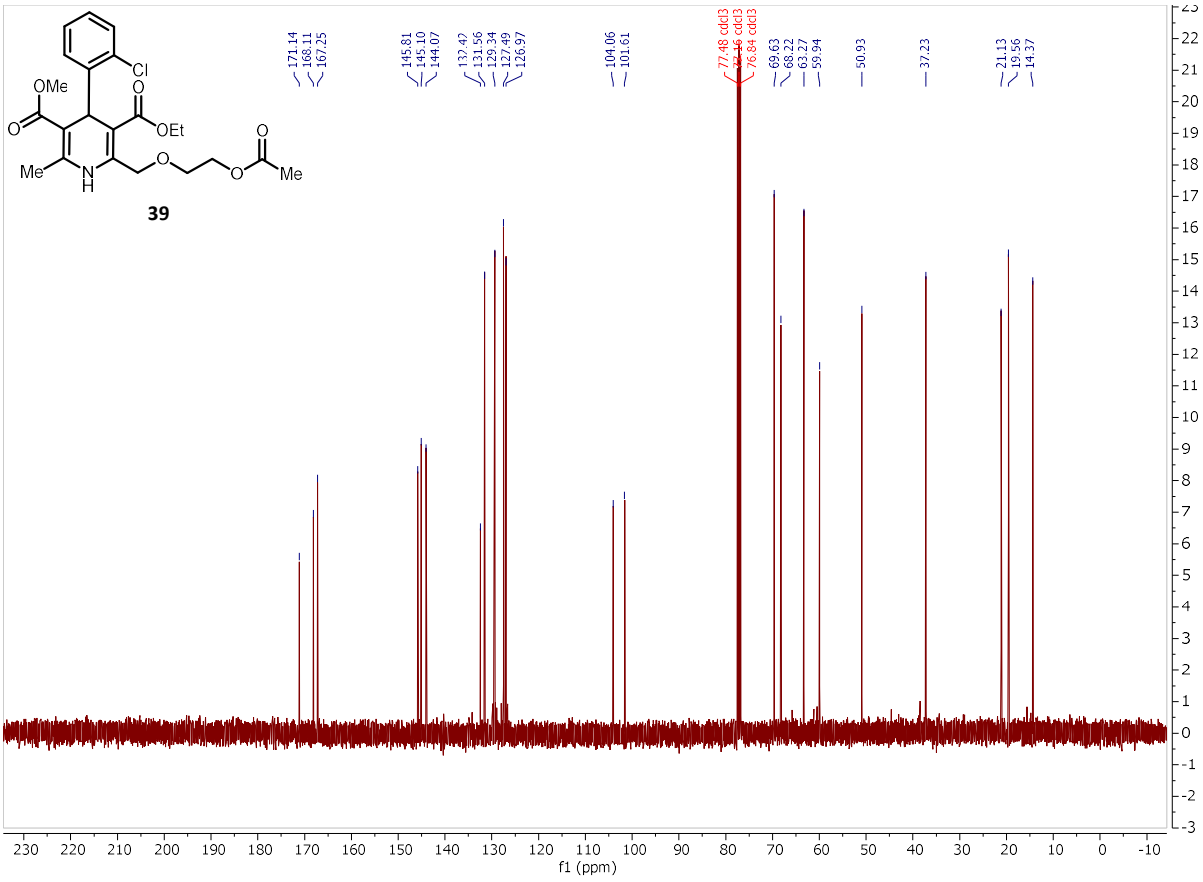
36

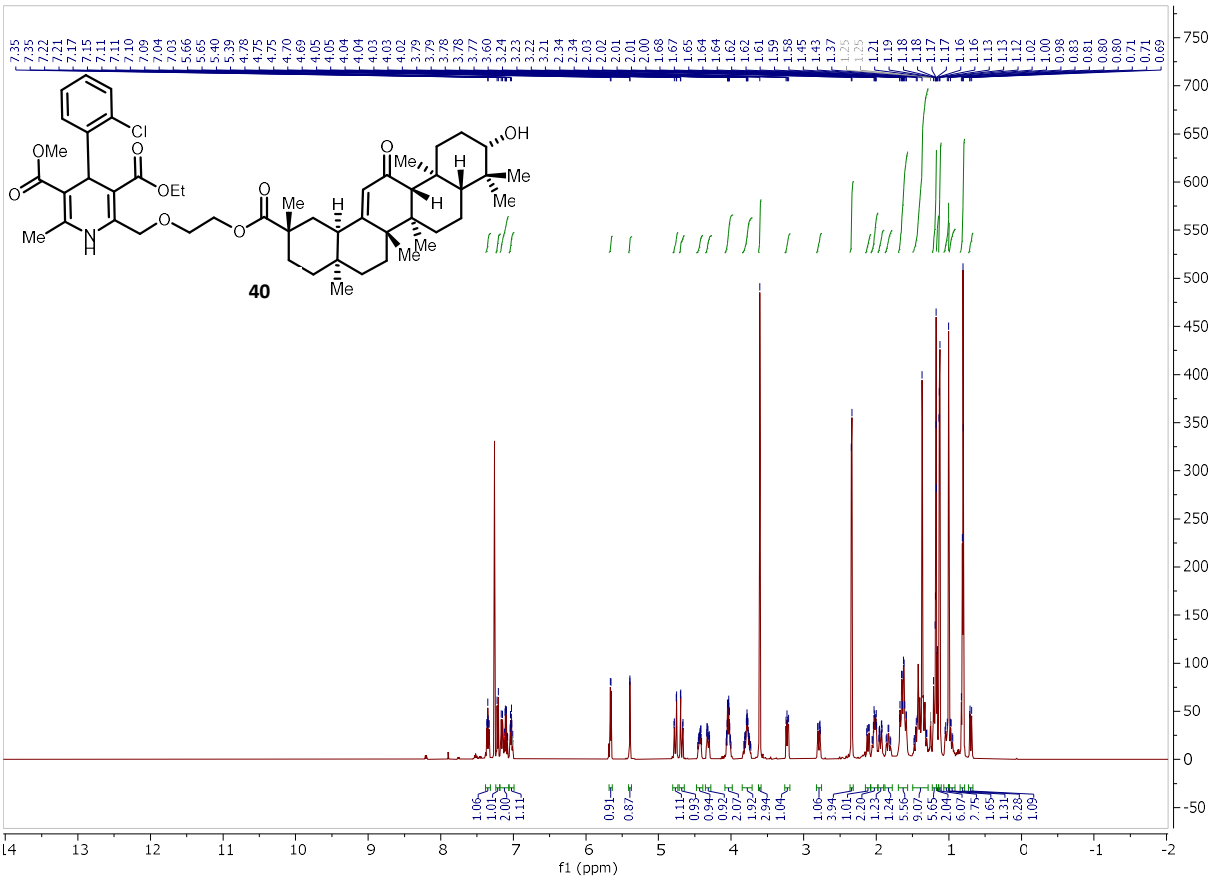

37
f1 (ppm)

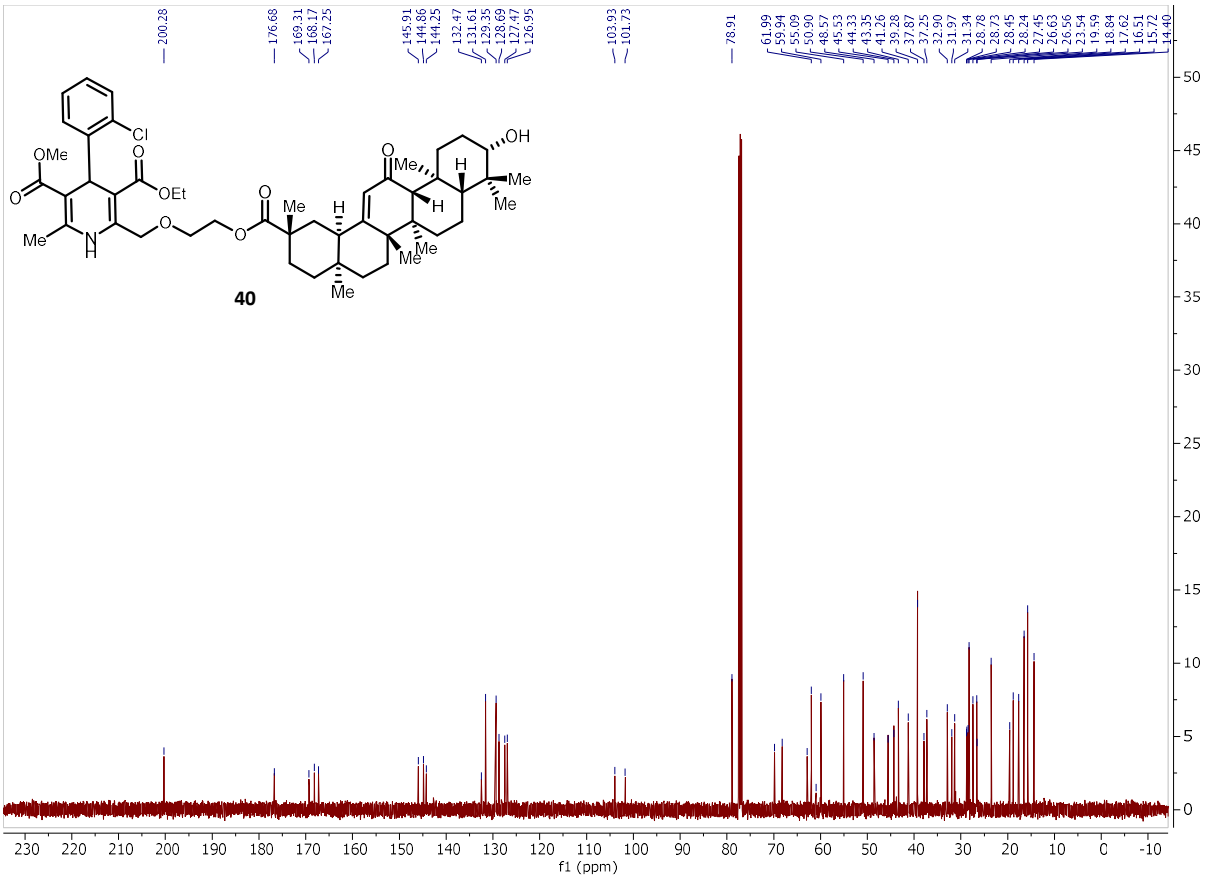

200.35
176.14
169.16
149.82
143.35
128.61
110.67
110.60
78.89
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
61.91
58.02
55.07
48.40
45.48
44.19
43.27
41.25
39.27
39.26
37.68
37.19
32.90
31.87
28.57
28.23
28.21
27.43
26.62
26.54
23.43
18.80
17.62
16.50
15.71
f1 (ppm)

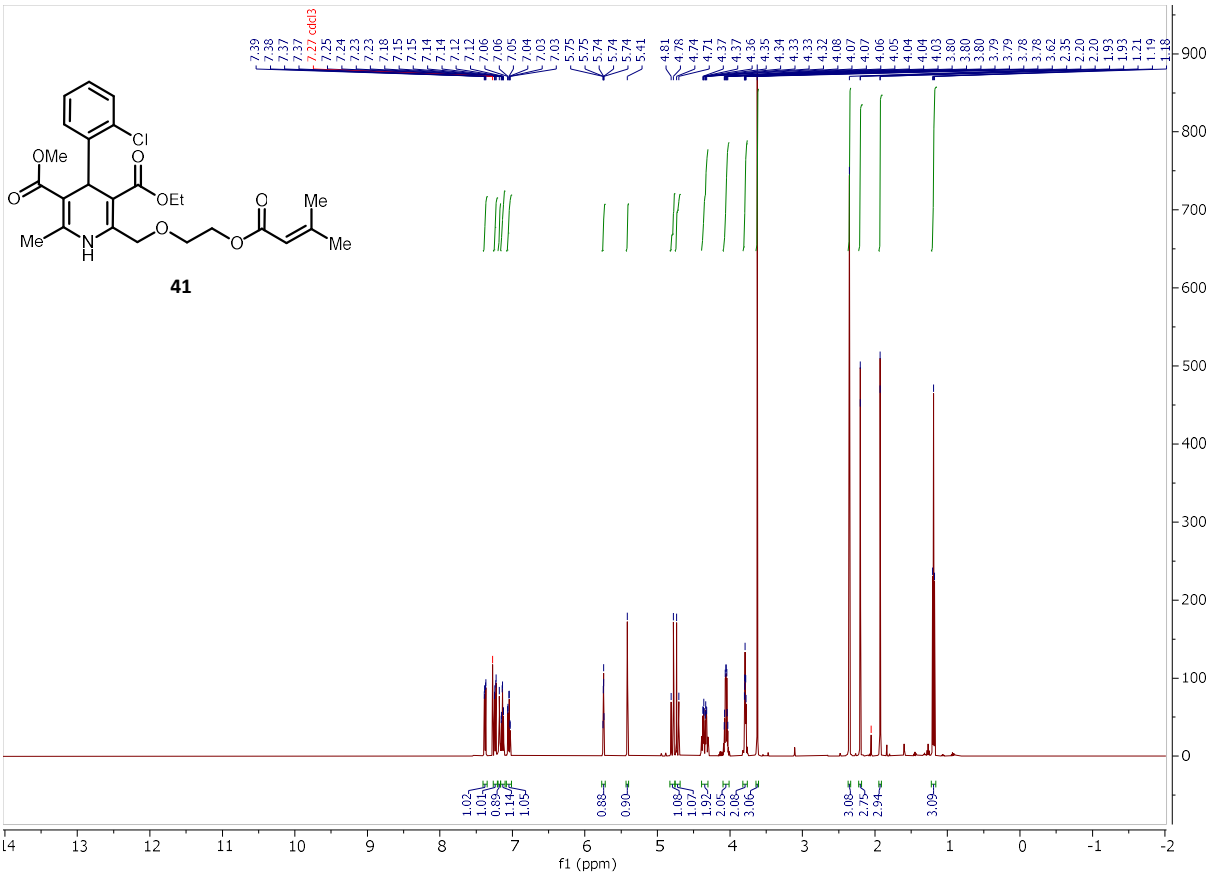
37

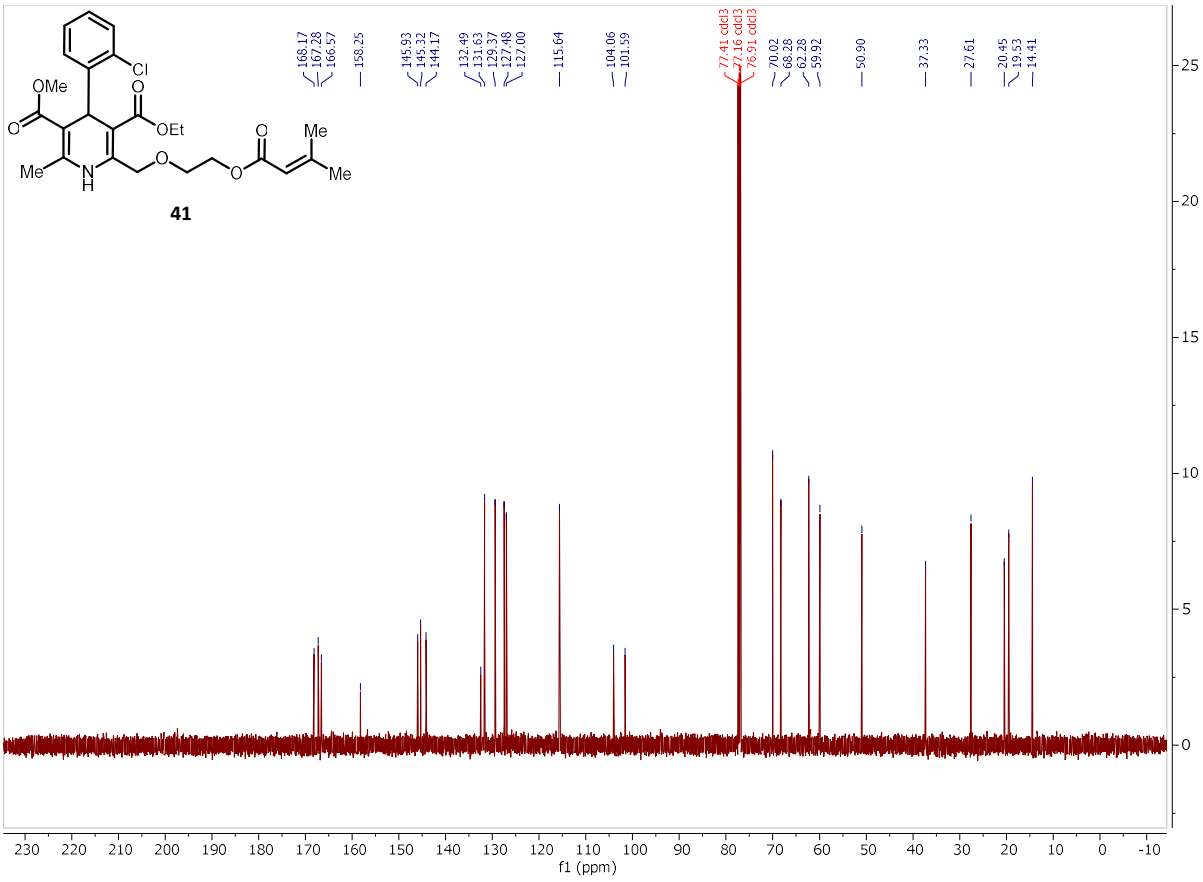

Cl
OMe
O
O
OEt
O
Me
N
H
O
O
Me
39
f1 (ppm)

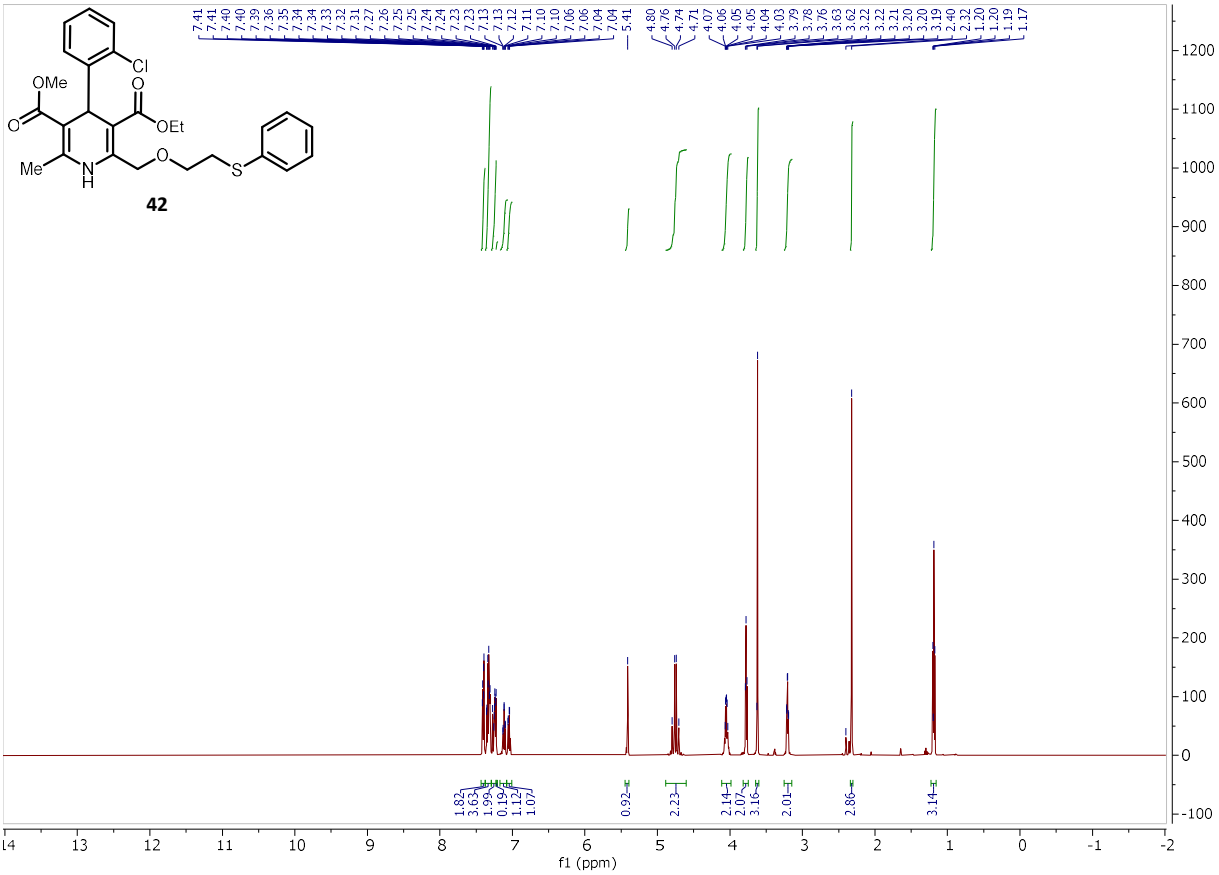

Cl
OMe
O
O
OEt
O
Me
N
H
O
O
Me
39
171.14
168.11
167.25
145.81
145.10
144.07
137.42
131.56
129.34
127.49
126.97
104.06
101.61
77.48 cdcl3
76.84 cdcl3
69.63
68.22
63.27
59.94
50.93
37.23
21.13
19.56
14.37
f1 (ppm)

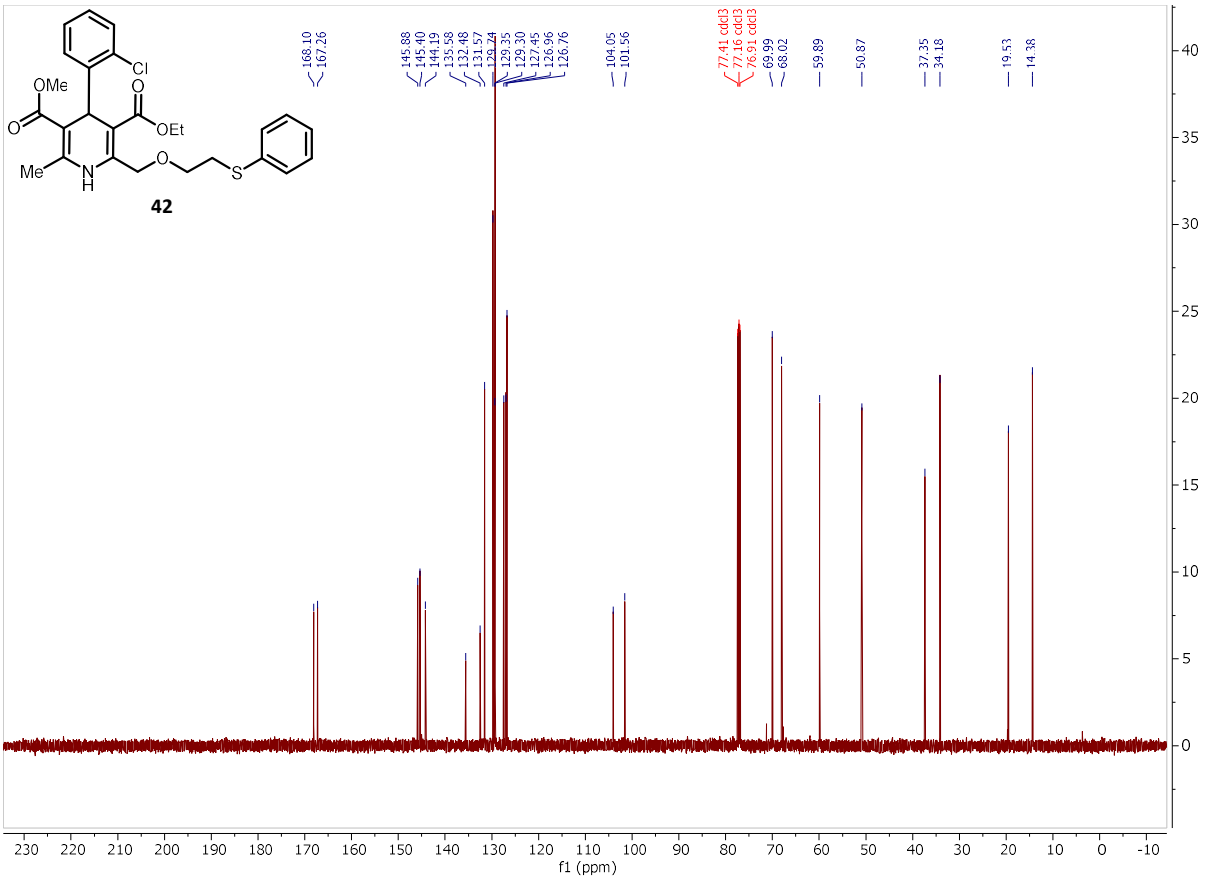

Cl
OMe
O
OEt
Me
N
H
O
Me
H
Me
Me
Me
O
Me
H
OH
Me
H
Me
40
f1 (ppm)


200.28
176.68
169.31
168.17
167.25
145.91
144.86
144.25
132.47
131.61
129.35
128.69
127.47
126.95
103.93
101.73
78.91
61.99
59.94
55.09
50.90
48.57
45.53
44.33
43.35
41.26
39.28
37.87
37.25
32.90
31.97
31.34
28.78
28.73
28.45
28.24
27.45
26.63
26.56
23.54
19.59
18.84
17.62
16.51
15.72
14.40
Cl
OMe
O
OEt
Me
N
H
O
Me
H
OH
Me
Me
Me
Me
Me
Me
40
f1 (ppm)


Cl
OMe
O
O
OEt
O
Me
Me
N
H
Me
41
f1 (ppm)


41
168.17
167.28
166.57
158.25
145.93
145.32
144.17
132.49
131.63
129.37
127.48
127.00
115.64
104.06
101.59
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
70.02
68.28
62.28
59.92
50.90
37.33
27.61
20.45
19.53
14.41
f1 (ppm)


Cl
OMe
O
O
OEt
Me
N
H
O
S
42
f1 (ppm)


Cl
OMe
O
O
OEt
Me
N
H
O
S
42
168.10
167.26
145.88
145.40
144.19
135.58
132.48
131.57
129.24
129.35
129.30
127.45
126.96
126.76
104.05
101.56
77.41 cdcl3
77.16 cdcl3
76.91 cdcl3
69.99
68.02
59.89
50.87
37.35
34.18
19.53
14.38
f1 (ppm)